

The background of the cover is a vibrant, abstract composition of laboratory glassware. It features several round-bottom flasks and beakers, some containing liquids of various colors like red, blue, and green. The lighting is bright and warm, creating a yellow-to-orange gradient across the entire image. The glassware is arranged in a way that suggests a chemical reaction or a laboratory setting.

e-book

Question Bank to Accompany

ESSENTIALS OF

Physical Chemistry



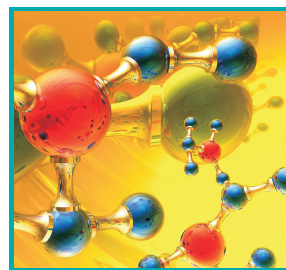
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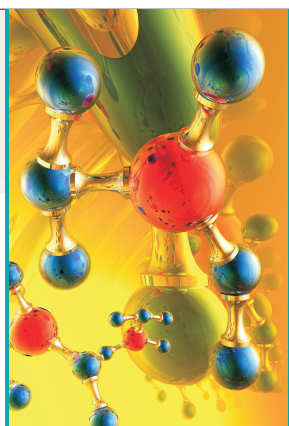
e-book

Question Bank to Accompany

Essentials of

PHYSICAL CHEMISTRY





Question Bank to Accompany Essentials of **PHYSICAL CHEMISTRY**

(A Textbook for B.Sc. Classes as per UGC Model Syllabus)

ARUN BAHL

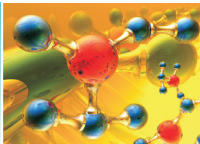
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e-book



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About this question bank

This Question Bank is a companion to the legendary textbook **Essentials of Physical Chemistry** by **Arun Bahl, B.S. Bahl and G.D. Tuli**. More than 100,00,00 students have used and learned Physical Chemistry from this book. The *Essentials of Physical Chemistry* has been a national Best-Seller for more than 65 years. This *e-book* has been written in response to repeated requests from a very large section of students and teachers.

This Question Bank is easy-to-use program that really prepares you for the exams. This *e-book* will be useful to those students who have difficulty analyzing numerical problems and find logical solutions and who have trouble with interpretation. It will also be useful to students who want additional problems and explanations in order to gain a better understanding of concepts.

Sharpen Skills

Boost Score

Build Ability

Gain Confidence

There is only one way to truly master the subject matter in Physical Chemistry—work out problems ! The more you work, the more you will learn. The grade you will receive will be reflection of your ability to solve problems. Also, be careful of how you use this *e-book*. The solutions contained in this *e-book* have been intended to provide explanations to help you understand the problem. Be sure to write out your answer to the problem first, and only then look it up to see if what you have done is correct.

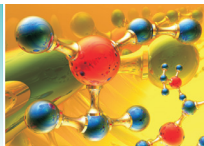
Each chapter in this *e-book* corresponds to the chapter of the *Essentials of Physical Chemistry* with the same number and title. Each chapter in this *e-book* is divided into 3 sections :

1. **Key Concepts and Equations.** These are intended to provide brief overview of the major points and topics presented in each chapter of the textbook.
2. **Additional New Solved Problems.** This Question Bank has over 600 new additional solved problems. These problems have been carefully selected from latest University Examinations and Entrance Tests.
3. **Additional Practice Problems.** This Question Bank provides more than 600 new practice problems with final answers. This section is designed to test the student's mastery of the material.

We urge you to study regularly, and hope that this Question Bank will make it easier for you to do so. Remember that the last minute studies never work !

Gaining a mastery of Physical Chemistry is hard work. It is hoped that this *e-book* will be helpful to you and that you will find your efforts rewarded.

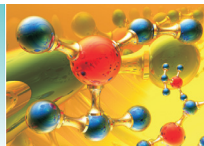
Arun Bahl



General tips on solving problems in Physical Chemistry

- ❑ Understanding concepts is the key to working problems. Read the book carefully and try to understand the relationships between various physical properties.
- ❑ Understand a problem before you try to work it. Read it carefully, and do not jump to conclusions. Do not run the risk of misinterpretation. Learn to recognize the type of problem.
- ❑ If you do not understand some words or terms in the problem, look up their meaning in the text of a dictionary. Do not just guess.
- ❑ In the case of problems that involve many words or a descriptive situation, rewrite the problem using a minimum number of words to express the bare-bones essence of the problem.
- ❑ Some problems give more information than is needed for the solution. Learn to pick out what is needed and ignore the rest.
- ❑ When appropriate, draw a simple sketch or diagram (with labels) to show how the different parts are related.
- ❑ Specifically pick out (a) What is given and (b) What is asked for.
- ❑ Look for a relationship (a conceptual principle or a mathematical equation) between what is given and what is asked for.
- ❑ Set up the problem in a concise, logical, stepwise manner, using units for all terms and factors.
- ❑ When a problem includes parentheses, do the operations inside the parentheses first.
- ❑ Think about your answer. See whether it is expressed in the units that were asked for, and whether it is reasonable in size for the information given. If not, check back and see if you can locate the trouble.





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1

Structure of Atom —Classical Mechanics

CHAPTER

KEY CONCEPTS AND EQUATIONS



FUNDAMENTAL PARTICLES

An atom consists of the two parts :

- Extremely small but dense central part called the nucleus.
- Extra nuclear part.

The size of nucleus is of the order 10^{-15} m and it contains positively charged **protons** and neutral particles called **neutrons**. These particles are collectively called **nucleons**.

The charge and mass of these fundamental particles are given in the Table 1.1.

TABLE 1.1. CHARGE AND MASS OF FUNDAMENTAL PARTICLES.				
Name of the particle	Charge in coulomb	Unit Charge	Mass (Kg)	Name of the Discoverer
Electron	-1.60×10^{-19}	- 1	9.10×10^{-31} kg	J.J. Thomson
Proton	$+ 1.60 \times 10^{-19}$	+ 1	1.672×10^{-27} kg	E. Goldstein
Neutron	0	0	1.674×10^{-27} kg	Chadwick

ATOMIC NUMBER AND MASS NUMBER

Atomic number is the number of protons present in the nucleus of the atom. It is also equal to the number of electrons in the neutral atom. It is denoted by Z.

Mass Number is the number of nucleons present in the nucleus of an atom. It is denoted by A. An atom is represented by A_ZX or ${}_ZX^A$. The difference between the mass number and atomic number gives the number of neutrons present in the atom, *i.e.*

$$\text{Number of neutrons} = A - Z$$

PLANCK'S QUANTUM THEORY

The quantum theory proposed by Max Planck in 1900 may be stated as :

- Atom absorbs or emits radiations in small units called quanta or photons of energy, *i.e.*

$$E = h \nu$$

where ν is the frequency of emitted radiations and h the Planck's constant. Its value is 6.62×10^{-27} erg sec or 6.62×10^{-34} J sec.

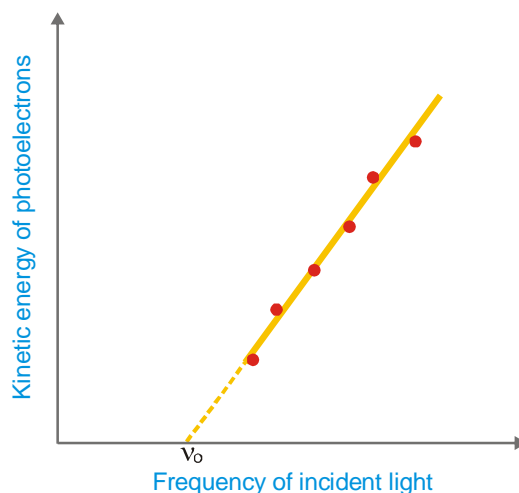
(b) An atom can emit or absorb energy equal to $nh\nu$ where n is a whole number.

PHOTOELECTRIC EFFECT

When electromagnetic radiations of sufficient energy are allowed to fall on metal surface such as caesium, sodium, etc., electrons are emitted. This phenomenon is called **photoelectric effect**. The frequency which provides enough energy just to release the electron from the metal surface is called **threshold energy**, ν_0 . For frequency less than ν_0 no electron will be emitted and for higher frequencies $\nu > \nu_0$, a part of the energy goes to knock the electron and remaining for imparting kinetic energy to the photoelectron emitted. Thus,

$$h\nu = h\nu_0 + \frac{1}{2}mv^2$$

where $h\nu$ is the energy of the photon of incident light, $h\nu_0$ is the minimum energy for an electron to escape from the metal and $\frac{1}{2}mv^2$ is the kinetic energy of the photoelectron. A graph between the kinetic energy of photoelectrons against the frequency of incident light is shown in Fig.1.1.



■ **Figure 1.1**
Kinetic energy of photoelectrons plotted against frequency of incident light.

EQUATIONS DERIVED FROM BOHR'S THEORY

To calculate the radius (r) and energy (E) of permissible orbits for one electron species, Bohr derived following equations :

$$\text{Angular momentum, } mvr = \frac{nh}{2\pi} \quad \dots \quad \text{(i)}$$

$$\text{Radius of an orbit, } r_n = \frac{n^2 h^2}{4\pi^2 m Z e^2} \quad \dots \quad \text{(ii)}$$

$$\text{Energy of an electron in } n\text{th orbit} \\ E_n = -\frac{2\pi^2 Z e^2}{nh} \quad \dots \quad \text{(iii)}$$

$$\text{Velocity of an electron in } n\text{th orbit} \\ v = \frac{2\pi Z e^2}{nh} \quad \dots \quad \text{(iv)}$$

In CGS units, m is the mass of an electron in grams, e its charge in esu, v its velocity in cm sec^{-1} , r the radius of the orbit in cm, h the Planck's constant, E the energy in ergs, Z the atomic number and n is the number of an integer having value 1,2,3 representing the first, second, third, orbits respectively.

For first orbit of H atom (or He^+ or Li^{2+} species) we have

$$r_1 = \frac{h^2}{4 \pi m Z e^2} \quad E_1 = - \frac{2 \pi^2 Z^2 e^4 m}{h^2} \quad \text{and} \quad v_1 = \frac{2 \pi e^2}{h}$$

and for n th orbit we have

$$r_n = n^2 \times r_1 \quad E_n = - \frac{E_1}{n^2} \quad \text{and} \quad v_n = \frac{v_1}{n}$$

The difference between two energy states n_2 (higher) to n_1 (lower) is given by

$$\Delta E = E_f - E_i$$

where E_f is the electronic energy in final state and E_i is the electronic energy in the initial state. Using Equation (iii) it can be shown that

$$\Delta E = - \frac{2 \pi^2 Z^2 e^4 m}{h^2} \left[\frac{1}{n_2^2} - \frac{1}{n_1^2} \right]$$

$$\text{or} \quad \Delta E = \frac{2 \pi^2 Z^2 e^4 m}{h^2} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$\text{or} \quad \frac{h c}{\lambda} = \frac{2 \pi^2 Z^2 e^4 m}{h^2} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$\text{or} \quad \frac{1}{\lambda} = \frac{2 \pi^2 Z^2 e^4 m}{c h^3} \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

where λ is the wavelength

$$\text{or} \quad \text{wave number } \bar{\nu} = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

$$\text{or} \quad R = \frac{2 \pi^2 e^4 m}{c h^3} \quad \left(\because Z = 1 \text{ for H atom} \right)$$

and R is called Rydberg constant. Its value is 109677 cm^{-1} or $1.09677 \times 10^{-7} \text{ m}$.

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. Calculate the velocity of the electron in the first Bohr orbit ($h = 6.625 \times 10^{-27} \text{ erg sec}$; $r = 0.529 \text{ \AA}$; $m = 9.109 \times 10^{-28} \text{ g}$).

SOLUTION :

Formula used

$$m v r = \frac{n h}{2 \pi}$$

$$\text{or} \quad v = \frac{n h}{2 \pi m r}$$

Quantities given

$$n = 1 \quad h = 6.625 \times 10^{-27} \text{ erg sec} \quad r = 0.529 \text{ \AA} = 0.529 \times 10^{-8} \text{ cm}$$

Substitution of values

$$\begin{aligned} \text{We have} \quad \nu &= \frac{1 \times 6.625 \times 10^{-27} \text{ erg sec}}{2 \times 3.14 \times (9.109 \times 10^{-28} \text{ g}) \times (0.529 \times 10^{-8} \text{ cm})} \\ &= 0.2189 \times 10^9 \text{ cm sec}^{-1} \\ &= \mathbf{2.189 \times 10^8 \text{ cm sec}^{-1}} \end{aligned}$$

SOLVED PROBLEM 2. Calculate the energy of transition involving $n_1 = 6$ to $n_2 = 3$ in a hydrogen atom, given that Rydberg constant $R = 109737.32 \text{ cm}^{-1}$ and $h = 6.63 \times 10^{-34} \text{ J sec}$.

SOLUTION :**Formula used**

$$\Delta E = \frac{h c}{\lambda}$$

$$\text{or} \quad = h c R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad \left(\because \frac{1}{\lambda} = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \right)$$

Quantities given

$$\begin{aligned} h &= 6.63 \times 10^{-34} \text{ J sec} & n_1 &= 6 & n_2 &= 3 \\ c &= 3 \times 10^{10} \text{ cm sec}^{-1} & R &= 109737.32 \text{ cm}^{-1} \end{aligned}$$

Substitution of values

$$\begin{aligned} \Delta E &= (6.63 \times 10^{-34} \text{ J sec}) \times (3 \times 10^{10} \text{ cm sec}^{-1}) \times (109737.32 \text{ cm}^{-1}) \left[\frac{1}{6^2} - \frac{1}{3^2} \right] \\ &= 2182675.295 \times 10^{-24} \left[\frac{1}{36} - \frac{1}{9} \right] \text{ J} \\ &= 2182675.295 \times 10^{-24} (-0.0833) \text{ J} \\ &= -181886.9 \times 10^{-24} \text{ J} \\ &= \mathbf{-1.819 \times 10^{-19} \text{ J}} \end{aligned}$$

SOLVED PROBLEM 3. Calculate the wavelength associated with an electron moving with a velocity of $1 \times 10^8 \text{ cm sec}^{-1}$. Mass of an electron = $9.1 \times 10^{-28} \text{ g}$.

SOLUTION :**Formula used**

$$\lambda = \frac{h}{m v}$$

Quantities given

$$m = 9.1 \times 10^{-28} \text{ g} \quad v = 1 \times 10^8 \text{ cm sec}^{-1} \quad h = 6.625 \times 10^{-27} \text{ erg sec}$$

Substitution of values

$$\begin{aligned} \text{We have} \quad \lambda &= \frac{6.625 \times 10^{-27} \text{ erg sec}}{(9.1 \times 10^{-28} \text{ g}) \times (1 \times 10^8 \text{ cm sec}^{-1})} \\ &= 0.728 \times 10^{-9} \text{ cm} \\ &= \mathbf{7.28 \times 10^{-10} \text{ cm}} \end{aligned}$$

SOLVED PROBLEM 4. Calculate the radius of third orbit of hydrogen atom ($h = 6.625 \times 10^{-27}$ erg sec; $m = 9.1091 \times 10^{-28}$ g; $e = 4.8 \times 10^{-10}$ esu).

SOLUTION :

Formula used

$$r = \frac{n^2 h^2}{4 \pi^2 m e^2}$$

Quantities given

$$n = 3$$

$$h = 6.625 \times 10^{-27} \text{ erg sec}$$

$$m = 9.1091 \times 10^{-28} \text{ g}$$

$$e = 4.8 \times 10^{-10} \text{ esu}$$

Substitution of values

$$\begin{aligned} \text{We have } r &= \frac{3^2 \times (6.625 \times 10^{-27} \text{ erg sec})^2}{4 \times (3.14)^2 \times (9.1091 \times 10^{-28} \text{ g}) \times (4.8 \times 10^{-10} \text{ esu})^2} \\ &= 0.04772 \times 10^{-6} \text{ cm} \\ &= \mathbf{4.772 \times 10^{-8} \text{ cm}} \end{aligned}$$

SOLVED PROBLEM 5. Calculate the wavelength of first line in Lyman series of hydrogen spectrum. (R, Rydberg constant = 109677 cm^{-1}).

SOLUTION :

$$\text{Formula used } \frac{1}{\lambda} = R Z^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

Quantities given

$$R = 109677 \text{ cm}^{-1}$$

$$Z = 1 \text{ (for hydrogen atom)}$$

$$n_1 = 1$$

$$n_2 = 2 \text{ (for 1st line in Lyman series)}$$

Substitution of values

$$\begin{aligned} \frac{1}{\lambda} &= 109677 \text{ cm}^{-1} \times \left[\frac{1}{1^2} - \frac{1}{2^2} \right] \\ &= 109677 \text{ cm}^{-1} \times 0.75 \\ &= 82257.75 \text{ cm}^{-1} \end{aligned}$$

or

$$\begin{aligned} \lambda &= \frac{1}{82257.75 \text{ cm}^{-1}} \\ &= 1.215 \times 10^{-5} \text{ cm} \\ &= 1.215 \times 10^{-5} \times 10^8 \text{ \AA} \\ &= \mathbf{1215 \text{ \AA}} \end{aligned}$$

SOLVED PROBLEM 6. In the photoelectric effect experiment irradiation of a metal with light of frequency $5 \times 10^{14} \text{ sec}^{-1}$ yields electrons with maximum kinetic energy $6.63 \times 10^{-14} \text{ J}$. Calculate ν_0 , threshold frequency of the metal.

SOLUTION :

Formula used

$$\begin{aligned} h \nu &= h \nu_0 + \frac{1}{2} m v^2 \\ \text{or K.E., } \frac{1}{2} m v^2 &= h \nu - h \nu_0 \\ &= h (\nu - \nu_0) \end{aligned}$$

Quantities given

$$KE = 6.63 \times 10^{-14} \text{ J} \quad \nu = 5 \times 10^{20} \text{ sec}^{-1} \quad h = 6.63 \times 10^{-34} \text{ J sec}$$

Substitution of values

$$6.63 \times 10^{-14} \text{ J} = 6.63 \times 10^{-34} \text{ J sec} \times (5 \times 10^{20} \text{ sec}^{-1} - \nu_0)$$

$$\begin{aligned} \text{or} \quad 5 \times 10^{20} \text{ sec}^{-1} - \nu_0 &= \frac{6.63 \times 10^{-14} \text{ J}}{6.63 \times 10^{-34} \text{ J sec}} \\ &= 1 \times 10^{20} \text{ sec}^{-1} \\ \nu_0 &= 5 \times 10^{20} \text{ sec}^{-1} - 1 \times 10^{20} \text{ sec}^{-1} \\ &= 4 \times 10^{20} \text{ sec}^{-1} \end{aligned}$$

SOLVED PROBLEM 7. The kinetic energy of a subatomic particle is $4.55 \times 10^{-25} \text{ J}$. Calculate the frequency of the particle wave. Planck's constant $h = 6.62 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$.

SOLUTION :**Formula used**

$$\text{Frequency, } \nu = \frac{m v^2}{h}$$

Quantities given

$$\begin{aligned} KE = \frac{1}{2} m v^2 &= 4.55 \times 10^{-25} \quad \text{or} \quad m v^2 = 2 \times 4.55 \times 10^{-25} \text{ J} \\ h &= 6.62 \times 10^{-34} \text{ J sec} \end{aligned}$$

Substitution of values

$$\begin{aligned} \text{We have} \quad \nu &= \frac{9.10 \times 10^{-25} \text{ J}}{6.62 \times 10^{-34} \text{ J sec}} \\ &= 1.37 \times 10^9 \text{ sec}^{-1} \end{aligned}$$

SOLVED PROBLEM 8. What is the frequency of emission spectrum when the electron in hydrogen atom falls from 5th to 2nd orbit ?

SOLUTION :**Formula used**

$$\Delta E = h c R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

Quantities given

$$\begin{aligned} n_1 &= 5 & n_2 &= 2 & h &= 6.625 \times 10^{-34} \text{ J sec} \\ c &= 3 \times 10^8 \text{ m sec}^{-1} & R &= 1.09677 \times 10^7 \text{ m}^{-1} \end{aligned}$$

Substitution of values

$$\begin{aligned} \Delta E &= (6.625 \times 10^{-34} \text{ J sec}) \times (3 \times 10^8 \text{ m sec}^{-1}) \times (1.09677 \times 10^7 \text{ m}^{-1}) \times \left[\frac{1}{5^2} - \frac{1}{2^2} \right] \\ &= 21.798 \times 10^{-34+8+7} \times (0.04 - 0.25) \text{ J} \\ &= -4.5776 \times 10^{-19} \text{ J} \end{aligned}$$

$$\begin{aligned} \text{Now} \quad \text{Frequency, } \nu &= \frac{\Delta E}{h} \\ &= - \frac{4.5776 \times 10^{-19} \text{ J}}{6.625 \times 10^{-34} \text{ J sec}} \\ &= - 0.6909 \times 10^{15} \text{ sec}^{-1} \\ &= - 6.909 \times 10^{14} \text{ sec}^{-1} \end{aligned}$$

The negative sign simply indicates the loss of energy.

SOLVED PROBLEM 9. Calculate the energy difference, frequency and wavelength of light emitted when the electron in a hydrogen atom undergoes transition from 4th energy level to 2nd energy level (Rydberg constant = $1.09677 \times 10^7 \text{ m}^{-1}$).

SOLUTION :

Formula used

$$\Delta E = h c R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

Quantities given

$$n_1 = 2 \quad n_2 = 4 \quad R = 1.09677 \times 10^7 \text{ m}^{-1} \quad c = 3 \times 10^8 \text{ m sec}^{-1}$$

Substitution of values

$$\begin{aligned} \Delta E &= \frac{(6.625 \times 10^{-34} \text{ J sec}^{-1}) \times (3 \times 10^8 \text{ m sec}^{-1}) \times (1.09677 \times 10^7 \text{ m}^{-1})}{\left(\frac{1}{2^2} - \frac{1}{4^2} \right)} \\ &= 21.798 \times 10^{-34+8+7} \times 0.1875 \text{ J} \\ &= \mathbf{4.087 \times 10^{-19} \text{ J}} \end{aligned}$$

Also frequency, $\nu = \frac{\Delta E}{h} = \frac{4.087 \times 10^{-19} \text{ J}}{6.625 \times 10^{-34} \text{ J sec}}$

$$= 0.6169 \times 10^{15} \text{ sec}^{-1}$$

$$= \mathbf{6.169 \times 10^{14} \text{ sec}^{-1}}$$

and wavelength, $\lambda = \frac{c}{\nu} = \frac{3 \times 10^8 \text{ m sec}^{-1}}{6.619 \times 10^{14} \text{ m}}$

$$= 0.4532 \times 10^{-6} \text{ m}$$

$$= \mathbf{4.532 \times 10^{-7} \text{ m}}$$

SOLVED PROBLEM 10. If the energy difference between the ground state of an atom and its excited state is $4.4 \times 10^{-19} \text{ J}$, what is the wavelength of the photon required to produce this transition ?

SOLUTION :

Formula used

$$\Delta E = \frac{h c}{\lambda}$$

or

$$\lambda = \frac{h c}{\Delta E}$$

Quantities given

$$\Delta E = 4.4 \times 10^{-19} \text{ J} \quad h = 6.625 \times 10^{-34} \text{ J sec} \quad c = 3 \times 10^8 \text{ m sec}^{-1}$$

Substitution of values

$$\begin{aligned} \lambda &= \frac{(6.625 \times 10^{-34} \text{ J sec}) \times (3 \times 10^8 \text{ m sec}^{-1})}{(4.4 \times 10^{-19} \text{ J})} \\ &= 4.517 \times 10^{-34+8+19} \text{ m} \\ &= \mathbf{4.517 \times 10^{-7} \text{ m}} \end{aligned}$$

SOLVED PROBLEM 11. The electron in a hydrogen atom revolves in the second orbit. Calculate (i) the energy of electron in this orbit (ii) radius of the second orbit and (iii) frequency and wavelength of the spectral line emitted when this electron jumps to the ground state.

SOLUTION : (i) To calculate the energy of electron in 2nd orbit

Formula used

$$E_n = \frac{2 \pi^2 m e^4}{n^2 h^2}$$

Quantities given

$$n = 2 \quad e = 4.80 \times 10^{-10} \text{ esu} \quad h = 6.625 \times 10^{-27} \text{ erg sec} \quad m = 9.1 \times 10^{-28} \text{ g}$$

Substitution of values

$$\begin{aligned} E_2 &= - \frac{2 \times (3.14)^2 \times (4.8 \times 10^{-10} \text{ esu})^4 \times (9.1 \times 10^{-28} \text{ g})}{2^2 \times (6.625 \times 10^{-27} \text{ erg sec})^2} \\ &= - 3594.59 \times 10^{-14} \text{ erg} \\ &= - 3.59459 \times 10^{-14} \text{ erg} \\ &= - \mathbf{3.5946 \times 10^{-11} \text{ erg}} \end{aligned}$$

(ii) To calculate the radius of 2nd orbit

Formula used

$$r_2 = \frac{n^2 h^2}{4 \pi^2 m e^2}$$

Quantities given

$$n = 2 \quad h = 6.625 \times 10^{-27} \text{ erg sec} \quad m = 9.1 \times 10^{-28} \text{ g} \quad e = 4.8 \times 10^{-10} \text{ esu}$$

Substitution of values

$$\begin{aligned} r_2 &= \frac{2^2 \times (6.625 \times 10^{-27} \text{ erg sec})^2}{4 \times (3.14)^2 \times (9.1 \times 10^{-28} \text{ g}) \times (4.8 \times 10^{-10} \text{ esu})^2} \\ &= 0.0212 \times 10^{-54+28+20} \text{ cm} \\ &= 0.0212 \times 10^{-6} \text{ cm} \\ &= 2.12 \times 10^{-8} \text{ cm} \\ &= \mathbf{2.12 \text{ \AA}} \end{aligned}$$

(iii) To calculate the frequency and wavelength of the line emitted

Formula used

$$\frac{1}{\lambda} = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

Quantities given

$$n_1 = 1 \quad n_2 = 2 \quad R = 109677 \text{ cm}^{-1}$$

Substitution of values

$$\begin{aligned} \frac{1}{\lambda} &= (109677 \text{ cm}^{-1}) \times \left[\frac{1}{1^2} - \frac{1}{2^2} \right] \\ &= 109677 \times 0.75 \text{ cm}^{-1} \\ &= 82257.75 \text{ cm}^{-1} \end{aligned}$$

or

$$\lambda = \frac{1}{82257.57 \text{ cm}^{-1}} = \mathbf{1.2157 \times 10^{-5} \text{ cm}}$$

and frequency, $\nu = \frac{c}{\lambda} = \frac{3 \times 10^{10} \text{ cm}}{1.2157 \times 10^{-5} \text{ cm}}$
 $= 2.4677 \times 10^{15} \text{ Hz}$

SOLVED PROBLEM 12. According to Bohr's theory, the electronic energy of the hydrogen atom in n th Bohr's orbit is given by $E_n = -\frac{21.76 \times 10^{-19} Z^2}{n^2} \text{ J}$. Calculate the longest wavelength of light that will be needed to remove an electrons from 3rd Bohr orbit of He^+ ion.

SOLUTION :

Formula used

$$E_n = -\frac{21.76 \times 10^{-19} Z^2}{n^2}$$

Quantities given

$$Z = 2$$

$$n = 3$$

Substitution of values

$$\begin{aligned} E_n &= -\frac{21.76 \times 10^{-19} \times 4}{9} \\ &= -9.671 \times 10^{-19} \text{ J} \end{aligned}$$

Thus the energy required to remove an electron from 3rd Bohr's orbit of He^+ ion is $9.671 \times 10^{-19} \text{ J}$.

SOLVED PROBLEM 13. What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition $n = 4$ to $n = 2$ of He^+ spectrum ?

SOLUTION :

Formula used

$$\frac{1}{\lambda} = RZ^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

Quantities given (for helium atom)

$$Z = 2$$

$$n_1 = 2$$

$$n_2 = 4$$

Substitution of values

$$\begin{aligned} \frac{1}{\lambda_1} &= R \times 4 \times \left[\frac{1}{4} - \frac{1}{16} \right] \\ &= \frac{4R \times 3}{16} \end{aligned}$$

Quantities given (for hydrogen atom)

$$Z = 1$$

Substitution of values

$$\frac{1}{\lambda_2} = R \times 1 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

since

$$\lambda_1 = \lambda_2$$

We have
$$\frac{4R \times 3}{16} = R \times \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

or
$$\left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] = \frac{3}{4}$$

This is possible if $n_1 = 1$ and $n_2 = 2$

Thus the transition $n_2 = 2$ to $n_1 = 1$ (Lyman series) in hydrogen atom has the same wavelength as the Balmer series transition $n_2 = 4$ to $n_1 = 2$ of He^+ spectrum.

SOLVED PROBLEM 14. Find out the number of waves made by a Bohr electron in one complete revolution in its 3rd orbit.

SOLUTION :

Formula used

$$m v r = \frac{n h}{2 \pi}$$

Quantities given

$$n = 3$$

Substitution of values

$$m v r = \frac{3 h}{2 \pi}$$

or

$$2 \pi r = \frac{3 h}{m v} \quad \left[\because \lambda = \frac{h}{m v} \right]$$

$$= 3 \lambda$$

Hence three times the wavelength of electron is equal to the circumference of 3rd orbit. So the electron makes three waves around 3rd orbit.

SOLVED PROBLEM 15. Iodine molecule dissociates after absorbing light of 4500 \AA . If one quantum radiation is absorbed by each molecule, calculate the kinetic energy of iodine atom. (Bond energy of $\text{I}_2 = 240 \times 10^3 \text{ kJ mol}^{-1}$).

SOLUTION :

Formula used

$$\Delta E = \frac{h c}{\lambda}$$

Quantities given

$$h = 6.625 \times 10^{-34} \text{ J sec}$$

$$c = 3 \times 10^8 \text{ m sec}^{-1} \quad \lambda = 4500 \text{ \AA} = 4500 \times 10^{-10} \text{ m}$$

Substitution of values

$$\Delta E = \frac{(6.625 \times 10^{-34} \text{ J sec}) \times (3 \times 10^8 \text{ m sec}^{-1})}{(4500 \times 10^{-10} \text{ m})}$$

$$= 4.416 \times 10^{-19} \text{ J}$$

$$\text{Now Bond energy of } \text{I}_2 \text{ per molecule} = \frac{240 \times 10^3}{\text{Avogadro's No.}} \text{ J/molecule}$$

$$= \frac{240 \times 10^3}{6.023 \times 10^{23}} \text{ J/molecule}$$

$$= 3.984 \times 10^{-19} \text{ J/molecule}$$

$$\begin{aligned} \text{Kinetic energy of iodine atoms} &= \text{Energy absorbed} - \text{Bond energy} \\ &= 4.416 \times 10^{-19} \text{ J} - 3.984 \times 10^{-19} \text{ J} \\ &= 0.432 \times 10^{-19} \text{ J} \end{aligned}$$

$$\begin{aligned} \therefore \text{Kinetic energy per iodine atom} &= \frac{0.432 \times 10^{-19}}{2} \text{ J} \\ &= 2.16 \times 10^{-20} \text{ J} \end{aligned}$$

SOLVED PROBLEM 16. Calculate the wave number for the shortest wavelength transition in the Balmer series of hydrogen atom.

SOLUTION :

Formula used

$$\bar{\nu} = \frac{1}{\lambda} = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

Quantities given

$$n_1 = 2$$

$$n_2 = \infty$$

$$R = 109677 \text{ cm}^{-1}$$

Substitution of values

$$\begin{aligned} \bar{\nu} &= 109677 \text{ cm}^{-1} \left[\frac{1}{2^2} - \frac{1}{\infty} \right] \\ &= 109677 \left[\frac{1}{4} - 0 \right] \text{ cm}^{-1} \\ &= 27419.25 \text{ cm}^{-1} \end{aligned}$$

SOLVED PROBLEM 17. Calculate the energy emitted when electrons of 1.0 g atom of hydrogen undergo transition giving the spectral line of lowest energy in the visible region of its atomic spectrum. ($R = 1.1 \times 10^7 \text{ m}^{-1}$).

SOLUTION :

Formula used

$$\frac{1}{\lambda} = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

Quantities given

$$R = 1.10 \times 10^7 \text{ m}^{-1}$$

For Balmer series $n_1 = 2$

For visible region we have Balmer series and

$n_2 = 3$ (lowest energy)

Substitution of values

$$\begin{aligned} \frac{1}{\lambda} &= 1.1 \times 10^7 \text{ m}^{-1} \times \left[\frac{1}{2^2} - \frac{1}{3^2} \right] \\ &= 1.1 \times 10^7 \text{ m}^{-1} \times \frac{5}{36} \\ &= 0.15277 \times 10^7 \text{ m}^{-1} \\ \text{or } \lambda &= \frac{1}{0.15277 \times 10^7 \text{ m}^{-1}} \\ &= 6.546 \times 10^{-7} \text{ m} \end{aligned}$$

To calculate energy emitted

Formula used

$$\Delta E = \frac{h c}{\lambda}$$

Quantities given

$$\lambda = 6.545 \times 10^{-7} \text{ m}$$

$$h = 6.625 \times 10^{-34} \text{ J sec}$$

$$c = 3 \times 10^8 \text{ m sec}^{-1}$$

Substitution of values

$$\Delta E = \frac{(6.625 \times 10^{-34} \text{ J sec}) \times (3 \times 10^8 \text{ m sec}^{-1})}{6.545 \times 10^{-7} \text{ m}}$$

$$= 3.037 \times 10^{-34+8+7} \text{ J}$$

$$= 3.037 \times 10^{-19} \text{ J}$$

Now energy emitted from 1 g atom of hydrogen

$$= 3.037 \times 10^{-19} \text{ J} \times \text{Avogadro's No.}$$

$$= 3.037 \times 10^{-19} \times 6.02 \times 10^{23} \text{ J}$$

$$= \mathbf{182.82 \text{ kJ}}$$

SOLVED PROBLEM 18. Calculate the wavelength of radiation emitted, producing a line in Lyman series, when an electron falls from fourth stationary state in hydrogen atom. ($R = 1.1 \times 10^7 \text{ m}^{-1}$)

SOLUTION :

Formula used

$$\frac{1}{\lambda} = R \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right]$$

Quantities given

$$n_2 = 4$$

$$n_1 = 1 \text{ (Lyman series)}$$

$$R = 1.1 \times 10^7 \text{ m}^{-1}$$

Substitution of values

$$\frac{1}{\lambda} = (1.1 \times 10^7 \text{ m}^{-1}) \times \left[\frac{1}{1^2} - \frac{1}{4^2} \right]$$

$$= 1.1 \times 10^7 \text{ m}^{-1} \times \left[1 - \frac{1}{16} \right]$$

$$= 1.1 \times 10^7 \times \frac{15}{16} \text{ m}^{-1}$$

$$= 1.0313 \times 10^7 \text{ m}^{-1}$$

$$= 1.0313 \times 10^7 \text{ m}^{-1}$$

or

$$\lambda = \frac{1}{1.0313 \times 10^7 \text{ m}^{-1}}$$

$$= 0.9696 \times 10^{-7}$$

$$= \mathbf{9.696 \times 10^{-8} \text{ m}}$$

ADDITIONAL PRACTICE PROBLEMS

- Calculate the velocity of the electron in the first Bohr's orbit ($h = 6.625 \times 10^{-27} \text{ erg sec}$; $r = 0.529 \text{ \AA}$; $m = 9.109 \times 10^{-28} \text{ g}$).
Answer. $2.189 \times 10^8 \text{ cm sec}^{-1}$
- Calculate the energy of transition involving $n_1 = 6$ to $n_2 = 3$ in a hydrogen atom given that Rydberg constant, $R = 109737.32 \text{ cm}^{-1}$ and $h = 6.63 \times 10^{-34} \text{ J sec}$.
Answer. $1.818 \times 10^{-19} \text{ J}$
- Calculate the radius of the third orbit of hydrogen atom ($h = 6.625 \times 10^{-27} \text{ erg sec}$; $m = 9.1091 \times 10^{-28} \text{ g}$; $e = 4.8 \times 10^{-10} \text{ esu}$).
Answer. 4.763×10^{-8}

4. Calculate the wavelength of the first line in Balmer series of hydrogen spectrum. ($R = 109677 \text{ cm}^{-1}$)
Answer. 1215 \AA
5. What is frequency of a red light source having wavelength of 700 nm (nanometer) ? Calculate the energy of a photon of light.
Answer. $4.28 \times 10^{14} \text{ sec}^{-1}$; $2.78 \times 10^{-19} \text{ J}$
6. What is the frequency of emission spectra when the electron in a hydrogen atom falls from n_6 orbit to n_2 orbit ?
Answer. $7.30 \times 10^{14} \text{ sec}^{-1}$
7. A light beam has a frequency of $1.0 \times 10^{12} \text{ Hertz}$. What is the wavelength of the beam in meters ? The velocity of light is $3.0 \times 10^8 \text{ m sec}^{-1}$.
Answer. $3.0 \times 10^4 \text{ m sec}^{-1}$
8. Sound waves travel about 203 m sec^{-1} in air. What is the wavelength of the sound produced by a tuning fork of 512 vibrations per second ?
Answer. 0.396 m
9. Calculate the loss of energy in Joules per mole of photons, when atoms release radiations at a frequency of 10^{12} sec^{-1} .
Answer. $4 \times 10^2 \text{ J mol}^{-1}$
10. An electron in an atom drops to a lower energy level with the release of $5.0 \times 10^{14} \text{ sec}^{-1}$ radiations. What is the loss of energy in J mol^{-1} ?
Answer. $2.0 \times 10^5 \text{ J mol}^{-1}$
11. Visible light is in the range of $4.0 \times 10^{14} \text{ Hz}$ to $7.5 \times 10^{14} \text{ Hz}$. Calculate the range of visible radiation in meters.
Answer. $4 \times 10^{-7} \text{ m}$ to $7.5 \times 10^{-7} \text{ m}$
12. In hydrogen atom the energy of the electron in first Bohr's orbit is $-1312 \times 10^5 \text{ J mol}^{-1}$. What is the energy required for the excitation of second Bohr's orbit ?
Answer. $9.84 \times 10^5 \text{ J mol}^{-1}$
13. The kinetic energy of an electron is $4.55 \times 10^{-25} \text{ J}$. Calculate its wavelength ($h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$; $m = 9.1 \times 10^{-31} \text{ kg}$)
Answer. $7.2 \times 10^{-7} \text{ m}$
14. The reaction $\text{I}_2 \xrightarrow{\text{energy}} 2 \text{I}$ was brought about by light radiation. It was found that 151 kJ mol^{-1} of light was required to dissociate the molecular iodine. Assuming that one quantum of light energy was required to dissociate one molecule of iodine, calculate the energy in Joules in one quantum of light and the wavelength of the light radiations in meters.
Answer. $2.51 \times 10^{-19} \text{ J}$; $7.92 \times 10^{-7} \text{ m}$
15. Using Bohr theory, calculate the radius and velocity of the electron in tenth orbit of hydrogen atom.
Answer. $0.53 \times 10^{-6} \text{ cm}$; $21.9 \times 10^7 \text{ cm sec}^{-1}$
16. Calculate the frequency and energy associated with photons of radiations having a wavelength of 6000 \AA . Planck's constant = $6.625 \times 10^{-27} \text{ erg sec}$.
Answer. $5 \times 10^{14} \text{ cps}$; $3.312 \times 10^{-27} \text{ erg}$
17. Calculate the range of frequencies of visible light (3800 \AA to 7600 \AA)
Answer. $3.948 \times 10^{14} \text{ cps}$ to $7.894 \times 10^{14} \text{ cps}$
18. Calculate the wave number of lines having frequency of $4.5 \times 10^{16} \text{ cps}$.
Answer. $1.5 \times 10^8 \text{ m}^{-1}$
19. Calculate the energy in kcal mol^{-1} of photons of an electromagnetic radiations of wavelength 4000 \AA .
Answer. $71.47 \text{ kcal mol}^{-1}$
20. Electromagnetic radiation of wavelength 242 nm is just sufficient to ionize the sodium atom. Calculate the ionization energy of sodium in kJ mol^{-1} ; $h = 6.6256 \times 10^{-34} \text{ Joule sec}$.
Answer. $494.5 \text{ kJ mol}^{-1}$
21. In a hydrogen atom, an electron jumps from 3rd orbit to first orbit. Find out the frequency and wavelength of the spectral line.

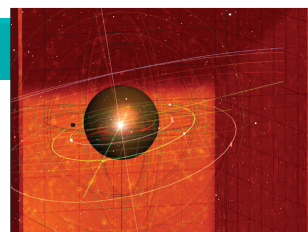
- Answer.** 1025.6 Å
22. Calculate the wavelength and energy of radiations emitted for the electronic transition from infinity (∞) to stationary state of the hydrogen atom. ($R = 1.09678 \times 10^7 \text{ m}^{-1}$; $h = 6.625 \times 10^{-34} \text{ Joule sec}$ and $c = 2.9979 \times 10^8 \text{ m sec}^{-1}$)
- Answer.** $9.11 \times 10^{-6} \text{ m}$; $217.9 \times 10^{-23} \text{ kJ}$
23. Calculate the wavelength in Å of the photon that is emitted when an electron in Bohr orbit $n = 2$ returns to the orbit $n = 1$ in the hydrogen atom. The ionization potential in the ground state of hydrogen atom is $2.17 \times 10^{-11} \text{ erg per atom}$.
- Answer.** 1220 Å
24. What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition $n = 4$ to $n = 2$ of He^+ transition ?
- Answer.** $n = 2$ to $n = 1$
25. A line at 434 nm in Balmer series of spectrum corresponds to a transition of an electron from the n th to 2nd Bohr orbit. What is the value of n ?
- Answer.** $n = 5$
26. The electron energy in hydrogen atom is given by $E = -21.7 \times 10^{-12}/n^2 \text{ ergs}$. Calculate the energy required to remove an electron completely from the $n = 2$ orbit. What is the longest wavelength (in cm) of light that can be used to cause this transition ?
- Answer.** $-5.42 \times 10^{-12} \text{ erg}$; $3.67 \times 10^{-5} \text{ cm}$
27. The energy transition in hydrogen atom occurs from $n = 3$ to $n = 2$ energy level. ($R = 1.097 \times 10^7 \text{ m}^{-1}$). (i) Calculate the wavelength of the emitted electron (ii) Will this electron be visible ? (iii) Which spectrum series does this photon belong to ?
- Answer.** 6564 Å ; Yes ; Balmer series
28. Calculate the energy emitted when electrons of 1.0 g of hydrogen undergo transition giving the spectral line of lowest energy in the visible region of its atomic spectrum ($R = 1.1 \times 10^7 \text{ m}^{-1}$; $c = 3 \times 10^8 \text{ m sec}^{-1}$; $h = 6.62 \times 10^{-34} \text{ J sec}$)
- Answer.** 182.5 kJ
29. The energy of the electron in the second and third Bohr orbits of the hydrogen atom is $-5.42 \times 10^{-12} \text{ erg}$ and $-2.41 \times 10^{-12} \text{ erg}$ respectively. Calculate the wavelength of the emitted radiation when the electron drops from third to second orbit.
- Answer.** 6600 Å
30. A doubly ionized lithium atom is hydrogen like with an atomic number 3. (i) Find the wavelength of the radiation required to excite the electron in Li from the first to third Bohr orbit (Ionization energy of hydrogen atom is 13.6 eV) (ii) How many spectral lines are observed in the emission spectrum of the above excited system ?
- Answer.** (i) 113.7 Å (ii) 3
31. An electron beam can undergo diffraction by crystals. Through what potential should a beam of electrons be accelerated so that its wavelength becomes equal to 1.54 Å.
- Answer.** 8.0459V
32. With what velocity should an α - particle travel towards the nucleus of a copper atom so as to arrive at a distance of 10^{-13} meter from the nucleus of the copper atom ?
- Answer.** $6.318 \times 10^6 \text{ m s}^{-1}$

2

Structure of the Atom —Wave Mechanics Approach

CHAPTER

KEY CONCEPTS AND EQUATIONS



WAVE MECHANICS

According to 'Wave Mechanical Theory' light exhibits both a wave and a particle nature under suitable conditions. This theory was further extended to matter *i.e.* electrons, protons and atoms. The new quantum mechanics which takes into account the particulate and wave nature of matter is termed as wave mechanics.

DE BROGLIE EQUATION

de Broglie in 1924 proposed that matter (atoms, neutrons, protons, electrons, etc.) has dual character *i.e.* it is associated with the properties of waves and their wavelengths λ is given by the relation

$$\lambda = \frac{h}{mv} = \frac{h}{\text{momentum}}$$

where m is the mass, v , the velocity of the particle and h the Planck's constant. de Broglie equation has no significance for large objects.

HEISENBERG'S UNCERTAINTY PRINCIPLE

It is impossible to measure simultaneously both the position and velocity (or momentum) of a microscopic particle with absolute accuracy or certainty. Mathematically,

$$\Delta x \times \Delta p \geq \frac{h}{4\pi}$$

or

$$\Delta x \times m \Delta v \geq \frac{h}{4\pi}$$

where Δx is uncertainty in position and Δp the uncertainty in momentum or Δv is the uncertainty in velocity and m the mass of the particle. It also has no significance for large objects.

SCHRÖDINGER'S WAVE EQUATION

Schrödinger derived an equation based upon the idea of the electron as 'standing wave' around the nucleus. This equation, known as Schrödinger's wave equation, is

$$\frac{d^2\psi}{dx^2} + \frac{d^2\psi}{dy^2} + \frac{d^2\psi}{dz^2} + \frac{8\pi^2m}{h^2} (E - PE) \psi = 0$$

where ψ is a mathematical function representing the amplitude of the wave, m the mass of the particle, v , the velocity, E the total energy of the particle, $P.E.$, the potential energy and x,y,z are three space coordinates.

It may be noted that square of the wave function, ψ^2 , represents the probability of finding the electron in different regions.

QUANTUM NUMBERS

According to modern theory of electronic structure an electron in an atom is specified in terms of four quantum numbers which describe the probable location of the electron. The values of quantum numbers govern its energy, orientation in space and its possible interaction with other electrons.

PRINCIPAL QUANTUM NUMBER

It denotes the principal shell to which the electron belongs. It also represents the average size of electron cloud. The distance of the electron from the nucleus in hydrogen atom is given by

$$r_n = 0.529 \times n^2 \text{ \AA}$$

where n is the principal quantum number. It can have integral values 1,2,3,4..... The maximum number of electrons in the principal shell is equal to $2n^2$.

AZIMUTHAL QUANTUM NUMBER

It describes the angular momentum of the electron and defines the shape of the orbital occupied by the electron. It is denoted by ' l ' and it can have all integral values from 0 to $n-1$. The total number of sublevels in each principal level is numerically equal to the principal quantum number of that level. For example,

$$\begin{array}{llll} n = 1 & l = 0 & & \\ n = 2 & l = 0, & l = 1 & \\ n = 3 & l = 0, & l = 1, & l = 2 \\ n = 4 & l = 0, & l = 1, & l = 2, & l = 3 \end{array}$$

The shape of the orbital is related to the azimuthal quantum number in the following manner :

$$\begin{array}{cccc} l=0 & l=1 & l=2 & l=3 \\ s\text{-subshell} & p\text{-subshell} & d\text{-subshell} & f\text{-subshell} \end{array}$$

MAGNETIC QUANTUM NUMBER

It accounts for the splitting of the spectral line in a magnetic field (Zeeman effect). It gives the orientation of the electron cloud and is denoted by m . For each value of l , m can have all integral values between $-l$ to $+l$ through zero. For example,

$$\begin{array}{llllll} l=0 & m=0 & & & & \\ l=1 & m=-1, & m=0, & m=+1 & & \\ l=2 & m=-2, & m=-1, & m=0, & m=+1, & m=+2 \\ l=3 & m=-3, & m=-2, & m=-1, & m=0, & m=+1, & m=+2, & m=+3 \end{array}$$

SPIN QUANTUM NUMBER

It accounts for the spin of the electron about its own axis. It is denoted by s and it can have either $+\frac{1}{2}$ or $-\frac{1}{2}$ value depending upon whether the electron spin is clockwise or anticlockwise. The summary of the four quantum numbers is given in Table 2.1.

TABLE 2.1 THE QUANTUM NUMBERS AND THEIR PERMITTED VALUES.

Quantum Number	Designation	Permitted Values
Principal Quantum Number	n	1,2,3,4,.....
Azimuthal Quantum Number	l	0,1,2,3,.....
Magnetic Quantum Number	m	$-l, \dots, 0, \dots, +l$
Spin Quantum Number	s	$+1/2$ or $-1/2$

PAULI'S EXCLUSION PRINCIPLE

No two electrons in an atom can have the same set of all the four identical quantum numbers. This means if two electrons have the same values for n , l and m , they must have different values of s . It helps us to find out the number of electrons that can be accommodated in an orbital or sublevel or principal energy level. The total number of electrons in first four energy shells are given in Table 2.2.

TABLE 2.2. MAXIMUM NUMBER OF ELECTRONS IN FIRST FOUR ENERGY LEVELS.

Principal Quantum Number	Number of electrons in				Total number of electrons
	s-subshell	p-subshell	d-subshell	f-subshell	
1	2	–	–	–	2
2	2	6	–	–	8
3	2	6	10	–	18
4	2	6	10	14	32

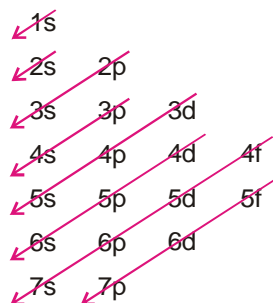
($n + l$) RULE

The energy of the electrons increases as the sum ($n+l$) increases, i.e. lower the value of ($n+l$) for an electron in an atom lower is its energy.

For two electrons with same ($n+l$) value, the one with lower value of n has lower energy.

AUFBAU PRINCIPLE

In the ground state of an atom, the electron enters the orbital of lowest energy first and subsequent electrons are added in the order of increasing energies. Fig. 2.1 shows the energy level scheme of filling up of electrons in various orbitals.



■ **Figure 2.1**
Aufbau order of filling up of electrons in various orbitals.

The increasing order of energy of various orbitals is as follows :

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s \dots\dots\dots$$

HUND'S RULE OF MAXIMUM MULTIPLICITY

Electrons are distributed among the orbitals of a subshell in such a way as to give maximum number of unpaired electrons with the same direction of spin.

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. A neutral atom has 2K, 8L and 3M electrons. Predict from this (i) its atomic number; (ii) total number of *s*-electrons; (iii) total number of *p*-electrons and (iv) total number of *d*-electrons.

SOLUTION :

(i) *Atomic number*

$$\begin{aligned} \text{Atomic number} &= \text{No. of Protons} &= \text{No. of electrons} \\ & &= 2 + 8 + 3 \\ & &= \mathbf{13} \end{aligned}$$

(ii) *Total number of s-electrons*

The electronic configuration of the atom with atomic number 13 is

$$\begin{array}{rcll} & 1s^2 & 2s^2 & 2p^6 & 3s^2 & 3p^1 \\ \text{Total no. of } s\text{-electrons} & = & 2 + 2 + 2 & & & [1s^2, 2s^2, 3s^2] \\ & = & \mathbf{6} & & & \end{array}$$

(iii) *Total no. of p-electrons*

$$\begin{array}{rcll} \text{Total no. of } p\text{-electrons} & = & 6 + 1 & & [2p^6, 3p^1] \\ & = & \mathbf{7} & & \end{array}$$

(iv) *Total no. of d-electrons*

$$\begin{array}{rcll} \text{Total no. of } d\text{-electrons} & = & \mathbf{0} & & [\because 3d \text{ is vacant}] \end{array}$$

SOLVED PROBLEM 2. The velocity of a ball bowled by Kapil Dev is 25 m sec^{-1} . Calculate the wavelength of the matter wave associated with the ball (mass of the cricket ball is 158.5 g ; $h = 6.625 \times 10^{-27} \text{ erg sec}$).

SOLUTION :

Formula used

$$\lambda = \frac{h}{m v}$$

Quantities given

$$m = 158.5 \text{ g} \qquad v = 25 \text{ m sec}^{-1} = 2500 \text{ cm sec}^{-1} \qquad h = 6.625 \times 10^{-27} \text{ erg sec}$$

Substitution of values

$$\begin{aligned} \lambda &= \frac{6.625 \times 10^{-27} \text{ erg sec}}{158.5 \text{ g} \times 2500 \text{ cm sec}^{-1}} \\ &= 0.0000167 \times 10^{-27} \text{ cm} \\ &= \mathbf{1.67 \times 10^{-32} \text{ cm}} \end{aligned}$$

SOLVED PROBLEM 3. Give the orbital configuration and number of unpaired electrons in the ground state for the following atoms :

- (i) Nitrogen (At. No. 7)
- (ii) Chlorine (At. No. 17)

(iii) Manganese (At. No. 25)

(iv) Cadmium (At. No. 48)

SOLUTION : The electronic configurations and number of unpaired electrons are as follows :

		No. of unpaired electrons
(i) Nitrogen (At. No. 7)	$= 1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$	3
(ii) Chlorine (At. No. 17)	$= 1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^1 3p_z^1$	1
(iii) Manganese (At. No. 25)	$= 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$	5
(iv) Cadmium (At. No. 48)	$= 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4s^2 4p^6 5s^2 4d^{10}$	0

SOLVED PROBLEM 4. A particle having wavelength of 6.6×10^{-4} cm is moving with a velocity of 10^6 cm sec⁻¹. Find the mass of the particle. (Planck's constant = 6.62×10^{-27} erg sec)**SOLUTION :****Formula used**

$$\lambda = \frac{h}{m v}$$

or

$$m = \frac{h}{v \lambda}$$

Quantities given

$$h = 6.62 \times 10^{-27} \text{ erg sec}$$

$$v = 10^6 \text{ cm sec}^{-1}$$

$$\lambda = 6.6 \times 10^{-4} \text{ cm}$$

Substitution of values

$$\begin{aligned} m &= \frac{6.62 \times 10^{-27} \text{ erg sec}}{6.6 \times 10^{-4} \text{ cm} \times 10^6 \text{ cm sec}^{-1}} \\ &= 1.003 \times 10^{-29} \text{ g} \end{aligned}$$

SOLVED PROBLEM 5. What is the wavelength associated with a particle of mass 0.1 g moving with a speed of 1×10^5 cm sec⁻¹? ($h = 6.6 \times 10^{-27}$ erg sec)**SOLUTION :****Formula used**

$$\lambda = \frac{h}{m v}$$

Quantities given

$$h = 6.6 \times 10^{-27} \text{ erg sec}$$

$$m = 0.1 \text{ g}$$

$$v = 1 \times 10^5 \text{ cm sec}^{-1}$$

Substitution of values

$$\begin{aligned} \lambda &= \frac{6.6 \times 10^{-27} \text{ erg sec}}{(0.1 \text{ g}) \times (1 \times 10^5 \text{ cm sec}^{-1})} \\ &= 66 \times 10^{-32} \text{ g} \\ &= 6.6 \times 10^{-31} \text{ g} \end{aligned}$$

SOLVED PROBLEM 6. Calculate the de Broglie wavelength for a ball of 200 g moving with a velocity 3×10^{10} cm sec⁻¹ and an electron moving with the same velocity. (Mass of electron = 9.109×10^{-28} g; $h = 6.624 \times 10^{-27}$ erg sec).**SOLUTION :****Formula used**

$$\lambda = \frac{h}{m v}$$

Quantities given**(i) For the ball**

$$m = 200 \text{ g}$$

$$v = 3 \times 10^{10} \text{ cm sec}^{-1}$$

$$h = 6.624 \times 10^{-27} \text{ erg sec}$$

Substitution of values

$$\begin{aligned}\lambda &= \frac{6.624 \times 10^{-27} \text{ erg sec}}{200 \text{ g} \times 3 \times 10^{10} \text{ cm sec}^{-1}} \\ &= \mathbf{1.04 \times 10^{-39} \text{ cm}}\end{aligned}$$

(ii) For the electron

$$m = 9.109 \times 10^{-28} \text{ g}$$

$$v = 3 \times 10^{10} \text{ cm sec}^{-1}$$

$$h = 6.624 \times 10^{-27} \text{ erg sec}$$

Substitution of values

$$\begin{aligned}\lambda &= \frac{6.624 \times 10^{-27} \text{ erg sec}}{9.109 \times 10^{-28} \text{ g} \times 3 \times 10^{10} \text{ cm sec}^{-1}} \\ &= 0.24239 \times 10^{-9} \text{ cm} \\ &= \mathbf{2.4239 \times 10^{-10} \text{ cm}}\end{aligned}$$

SOLVED PROBLEM 7. If an electron is accelerated by 100 volts, calculate the de Broglie wavelength associated with it. Also calculate the velocity acquired by the electron. (Mass of electron = $9.1 \times 10^{-28} \text{ g}$; $h = 6.62 \times 10^{-27} \text{ erg sec}$).

SOLUTION :**(i) To calculate wavelength****Formula used**

$$\lambda = \sqrt{\frac{150}{V \text{ volts}}} \text{ \AA}$$

Quantities given

$$V = 100 \text{ volts}$$

Substitution of values

$$\begin{aligned}\lambda &= \sqrt{\frac{150}{100}} \text{ \AA} \\ &= \sqrt{1.5} \text{ \AA} \\ &= 1.2247 \text{ \AA} \\ &= \mathbf{1.2247 \times 10^{-8} \text{ cm}}\end{aligned}$$

(ii) To calculate the velocity**Formula used**

$$\lambda = \frac{h}{m v}$$

or

$$v = \frac{h}{m \lambda}$$

Quantities given

$$m = 9.1 \times 10^{-28} \text{ g}$$

$$h = 6.62 \times 10^{-27} \text{ erg sec}$$

$$\lambda = 1.2247 \times 10^{-8} \text{ cm}$$

Substitution of values

$$\begin{aligned} v &= \frac{6.62 \times 10^{-27} \text{ erg sec}}{(9.1 \times 10^{-28} \text{ g}) \times (1.2247 \times 10^{-8} \text{ cm})} \\ &= 0.594 \times 10^9 \text{ cm sec}^{-1} \\ &= \mathbf{5.94 \times 10^8 \text{ cm sec}^{-1}} \end{aligned}$$

SOLVED PROBLEM 8. Calculate the wavelength of a particle of mass 1.5 g moving with a velocity of 250 m sec^{-1} .

SOLUTION :

Formula used

$$\lambda = \frac{h}{m v}$$

Quantities given

$$h = 6.625 \times 10^{-27} \text{ erg sec} \quad m = 1.5 \text{ g} \quad v = 250 \text{ m sec}^{-1} = 25000 \text{ cm sec}^{-1}$$

Substitution of values

$$\begin{aligned} \lambda &= \frac{6.625 \times 10^{-27} \text{ erg sec}}{1.5 \text{ g} \times 25000 \text{ cm sec}^{-1}} \\ &= 0.1766 \times 10^{-27-3} \text{ cm} \\ &= 0.1766 \times 10^{-30} \text{ cm} \\ &= \mathbf{1.766 \times 10^{-31} \text{ cm}} \end{aligned}$$

SOLVED PROBLEM 9. Calculate the wavelength of an electron of mass $9.1 \times 10^{-28} \text{ g}$ moving with a velocity of $4.2 \times 10^6 \text{ cm sec}^{-1}$ ($h = 6.62 \times 10^{-27} \text{ erg sec}$).

SOLUTION :

Formula used

$$\lambda = \frac{h}{m v}$$

Quantities given

$$h = 6.62 \times 10^{-27} \text{ erg sec} \quad m = 9.1 \times 10^{-28} \text{ g} \quad v = 4.2 \times 10^6 \text{ cm sec}^{-1}$$

Substitution of values

$$\begin{aligned} \lambda &= \frac{6.62 \times 10^{-27} \text{ erg sec}}{(9.1 \times 10^{-28} \text{ g}) \times (4.2 \times 10^6 \text{ cm sec}^{-1})} \\ &= 0.1732 \times 10^{-27+28-6} \text{ cm} \\ &= 0.1732 \times 10^{-5} \text{ cm} \\ &= 1.732 \times 10^{-6} \text{ cm} \\ &= \mathbf{1.732 \times 10^{-8} \text{ m}} \end{aligned}$$

SOLVED PROBLEM 10. Calculate the momentum of a particle which has de Broglie's wavelength of 0.10 nm . ($h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$).

SOLUTION :

Formula used

$$\lambda = \frac{h}{m v}$$

or

momentum,

$$m v = \frac{h}{\lambda}$$

Quantities given

$$h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1} \quad \lambda = 0.1 \times 10^9 \text{ m}$$

Substitution of values

$$\begin{aligned} \text{Momentum} &= \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}}{0.1 \times 10^{-9} \text{ m}} \\ &= \mathbf{6.6 \times 10^{-24} \text{ kg m sec}^{-1}} \end{aligned}$$

SOLVED PROBLEM 11. An electron is moving with a kinetic energy of $4.55 \times 10^{-25} \text{ J}$. Calculate de Broglie wavelength for it. (mass of the electron = $9.1 \times 10^{-31} \text{ kg}$; $h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$).

SOLUTION :**(i) To calculate the velocity of the electron****Formula used**

$$K.E. = \frac{1}{2} m v^2$$

or

$$v^2 = \frac{2 \times K.E.}{m}$$

Quantities given

$$K.E. = 4.55 \times 10^{-25} \text{ J} \quad m = 9.1 \times 10^{-31} \text{ kg}$$

Substitution of values

$$\begin{aligned} v^2 &= \frac{2 \times 4.55 \times 10^{-25} \text{ kg m}^2 \text{ sec}^{-2}}{9.1 \times 10^{-31} \text{ kg}} \\ &= 1 \times 10^6 \text{ m}^2 \text{ sec}^{-2} \end{aligned}$$

or

$$\begin{aligned} v &= \sqrt{1 \times 10^6 \text{ m}^2 \text{ sec}^{-2}} \\ &= 1 \times 10^3 \text{ m sec}^{-1} \end{aligned}$$

(ii) To calculate the wavelength of the electron**Formula used**

$$\lambda = \frac{h}{m v}$$

Quantities given

$$h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1} \quad m = 9.1 \times 10^{-31} \text{ kg} \quad v = 1 \times 10^3 \text{ m sec}^{-1}$$

Substitution of values

$$\begin{aligned} \lambda &= \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}}{9.1 \times 10^{-31} \text{ kg} \times 1 \times 10^3 \text{ m sec}^{-1}} \\ &= 0.7253 \times 10^{-34+31-3} \text{ m} \\ &= 0.7253 \times 10^{-6} \text{ m} \\ &= 7.253 \times 10^{-7} \text{ m} \\ &= \mathbf{725.3 \text{ nm}} \end{aligned}$$

SOLVED PROBLEM 12. Calculate the de Broglie's wavelength of an electron travelling with a speed of 20% of light.

SOLUTION :**Formula used**

$$\lambda = \frac{h}{m v}$$

Quantities given

$$h = 6.625 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1} \quad m = 9.1 \times 10^{-31} \text{ kg}$$

$$v = 20\% \text{ of } c = \frac{20 \times 3 \times 10^8}{100} \text{ m sec}^{-1} = 0.6 \times 10^8 \text{ m sec}^{-1}$$

Substitution of values

$$\begin{aligned}\lambda &= \frac{6.625 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}}{(9.1 \times 10^{-31} \text{ kg}) \times (0.6 \times 10^8 \text{ m sec}^{-1})} \\ &= 1.2133 \times 10^{-34+31-8} \text{ m} \\ &= 1.2133 \times 10^{-11} \text{ m} \\ &= 12.133 \times 10^{-12} \text{ m} \\ &= \mathbf{12.133 \text{ pm}} \quad [\because 1 \text{ pm} = 10^{-12} \text{ m}]\end{aligned}$$

SOLVED PROBLEM 13. Compare the relative de Broglie wavelength of an atom of hydrogen and an atom of oxygen both moving with the same velocity.

SOLUTION :

Formula used

$$\lambda = \frac{h}{m v}$$

$$\text{For hydrogen atom} \quad \lambda_1 = \frac{h}{m_1 v} \quad \dots (i)$$

$$\text{For oxygen atom} \quad \lambda_2 = \frac{h}{m_2 v} \quad [\because v \text{ is the same}] \dots (ii)$$

Dividing (i) by (ii), we have

$$\begin{aligned}\frac{\lambda_1}{\lambda_2} &= \frac{h}{m_1 v} \times \frac{m_2 v}{h} \\ &= \frac{m_2}{m_1}\end{aligned}$$

$$\text{or} \quad \frac{\lambda_1}{\lambda_2} = \frac{16 m_1}{m_1} \quad [\because \text{at. mass of O} = 16 \times \text{at. mass of H}]$$

$$\text{or} \quad \lambda_1 : \lambda_2 = 16 : 1$$

SOLVED PROBLEM 14. A good baseball pitcher can throw a 130 g baseball at a speed of 92 km hr⁻¹. What is the de Broglie wavelength in meters produced by the moving baseball ?

SOLUTION :

Formula used

$$\lambda = \frac{h}{m v}$$

Quantities given

$$h = 6.625 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$$

$$m = 130 \text{ g} = 130 \times 10^{-3} \text{ kg}$$

$$v = 92 \text{ km hr}^{-1} = 92 \times \frac{5}{18} \text{ m sec}^{-1}$$

$$[\because 1 \text{ km hr}^{-1} = \frac{5}{18} \text{ m sec}^{-1}]$$

Substitution of values

$$\begin{aligned}\lambda &= \frac{6.625 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}}{(130 \times 10^{-3} \text{ kg}) \times (25.55 \text{ m sec}^{-1})} \\ &= 0.001994 \times 10^{-34+3} \text{ m} \\ &= 0.001994 \times 10^{-31} \text{ m} \\ &= \mathbf{1.994 \times 10^{-34} \text{ m}}\end{aligned}$$

SOLVED PROBLEM 15. Calculate the product of uncertainty of displacement and velocity of a moving electron having a mass of 9.1×10^{-31} kg ($h = 6.6 \times 10^{-34}$ kg m² sec⁻¹).

SOLUTION :

Formula used

$$\Delta x \times m \Delta v = \frac{h}{4\pi}$$

or

$$\Delta x \times \Delta v = \frac{h}{4\pi m}$$

Quantities given

$$h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$$

$$m = 9.1 \times 10^{-31} \text{ kg}$$

Substitution of values

$$\begin{aligned} \Delta x \times \Delta v &= \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}}{4 \times 9.1 \times 10^{-31} \text{ kg} \times 3.14} \\ &= 0.05774 \times 10^{-34+31} \text{ m}^2 \text{ sec}^{-1} \\ &= \mathbf{5.774 \times 10^{-5} \text{ m}^2 \text{ sec}^{-1}} \end{aligned}$$

SOLVED PROBLEM 16. Calculate the certainty in position of an electron if uncertainty in velocity is 5.7×10^5 m sec⁻¹. ($h = 6.6 \times 10^{-34}$ kg m² sec⁻¹; mass of electron = 9.1×10^{-31} kg).

SOLUTION :

Formula used

$$\Delta x \times m \Delta v = \frac{h}{4\pi}$$

or

$$\Delta x = \frac{h}{4\pi m \Delta v}$$

Quantities given

$$h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$$

$$m = 9.1 \times 10^{-31} \text{ kg}$$

$$\Delta v = 5.7 \times 10^5 \text{ m sec}^{-1}$$

Substitution of values

$$\begin{aligned} \Delta x &= \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}}{4 \times 3.1 \times 9.1 \times 10^{-31} \text{ kg} \times 5.7 \times 10^5 \text{ m sec}^{-1}} \\ &= 0.0103 \times 10^{-34+31-5} \text{ m} \\ &= 0.0103 \times 10^{-8} \text{ m} \\ &= \mathbf{1.03 \times 10^{-10} \text{ m}} \end{aligned}$$

SOLVED PROBLEM 17. What are the possible l and m quantum numbers for an electron $n = 3$ quantum level of an atom ?

SOLUTION :

Here $n = 3$

$$\therefore l = 0, 1 \text{ and } 2$$

$$[\because l = 0, 1, \dots, n-1]$$

and when $l = 0 \quad m = 0$

$$l = 1 \quad m = -1, 0, +1$$

$$l = 2 \quad m = -2, -1, 0, +1, +2$$

SOLVED PROBLEM 18. The electronic configuration of an atom in the ground state is $1s^2 2s^2 2p^6$. Give the four quantum numbers of the electron in last orbital.

SOLUTION :

The given electron configuration is $1s^2 2s^2 2p^6$

or $1s^2 2s^2 2p_x^2 2p_y^2 2p_z^2$

∴ The last electron is in $2p_z$ orbital

For $2p_z$ orbital $n = 2, \quad l = 1, \quad m = 1$ and

$s = +\frac{1}{2}$ or $-\frac{1}{2}$

SOLVED PROBLEM 19. Arrange the electrons in the following list in order of increasing energy.

	n	l	m	s
(a)	3	2	-1	$+\frac{1}{2}$
(b)	4	0	0	$-\frac{1}{2}$
(c)	4	1	1	$+\frac{1}{2}$
(d)	2	1	-1	$-\frac{1}{2}$

SOLUTION :

$(n + l)$ values in respect of above electrons are

(a) $3 + 2 = 5$

(b) $4 + 0 = 4$

(c) $4 + 1 = 5$

(d) $2 + 1 = 3$

∴ Increasing order of energy is (d) < (b) < (a) < (c)

SOLVED PROBLEM 20. Deduce the possible set of four quantum number when $n = 3$

SOLUTION :

For $n = 3$ $l = 0, 1$ and 2

When	$l = 0$	$m = 0$	$s = +\frac{1}{2}$ or $-\frac{1}{2}$
	$l = 1$	$m = -1$	$s = +\frac{1}{2}$ or $-\frac{1}{2}$
		$m = 0$	$s = +\frac{1}{2}$ or $-\frac{1}{2}$
		$m = +1$	$s = +\frac{1}{2}$ or $-\frac{1}{2}$
	$l = 2$	$m = -2$	$s = +\frac{1}{2}$ or $-\frac{1}{2}$
		$m = -1$	$s = +\frac{1}{2}$ or $-\frac{1}{2}$
		$m = 0$	$s = +\frac{1}{2}$ or $-\frac{1}{2}$
		$m = +1$	$s = +\frac{1}{2}$ or $-\frac{1}{2}$
		$m = +2$	$s = +\frac{1}{2}$ or $-\frac{1}{2}$

SOLVED PROBLEM 21. Arrange the electrons represented by the following sets of quantum numbers in the decreasing order of energy.

$$(a) \quad n = 4 \quad l = 0 \quad m = 0 \quad s = +\frac{1}{2}$$

$$(b) \quad n = 3 \quad l = 1 \quad m = 0 \quad s = -\frac{1}{2}$$

$$(c) \quad n = 3 \quad l = 2 \quad m = 0 \quad s = +\frac{1}{2}$$

$$(d) \quad n = 3 \quad l = 0 \quad m = 0 \quad s = -\frac{1}{2}$$

SOLUTION :

The $(n + l)$ values of above electrons are as follows :

$$(a) \quad n = 4 \quad l = 0 \quad m = 0 \quad s = +\frac{1}{2} \quad n + l = 4 \quad (4s)$$

$$(b) \quad n = 3 \quad l = 1 \quad m = 0 \quad s = -\frac{1}{2} \quad n + l = 4 \quad (3p)$$

$$(c) \quad n = 3 \quad l = 2 \quad m = 0 \quad s = +\frac{1}{2} \quad n + l = 5 \quad (3d)$$

$$(d) \quad n = 3 \quad l = 0 \quad m = 0 \quad s = -\frac{1}{2} \quad n + l = 3 \quad (3s)$$

Thus the decreasing order of energy is $3d > 4s > 3p > 3s$

SOLVED PROBLEM 22. Calculate the wavelength of a 200 kg drum rolling at a speed of 30 km per hour.

SOLUTION :

Formula used

$$\lambda = \frac{h}{m v}$$

Quantities given

$$h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1} \quad m = 200 \text{ kg} \quad v = 30 \text{ km hr}^{-1} = \frac{30 \times 10^3}{60 \times 60} \text{ m sec}^{-1} \\ = 8.33 \text{ m sec}^{-1}$$

Substitution of values

$$\lambda = \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}}{200 \text{ kg} \times 8.33 \text{ m sec}^{-1}} \\ = 3.96 \times 10^{-37} \text{ m}$$

SOLVED PROBLEM 23. Calculate the momentum of a particle which has a de Broglie wavelength of 110 \AA .

SOLUTION :

Formula used

$$\lambda = \frac{h}{m v}$$

or

$$m v = \frac{h}{\lambda}$$

Quantities given

$$h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1} \quad \lambda = 110 \text{ \AA} = 110 \times 10^{-10} \text{ m}$$

Substitution of values

$$m v = \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}}{110 \times 10^{-10} \text{ m}} \\ = 6 \times 10^{-26} \text{ kg m sec}^{-1}$$

SOLVED PROBLEM 24. By applying de Broglie's equation, calculate wavelength associated with the motion of the earth, a ball and an electron. Following data is given :

$$\text{Mass of earth} = 6.0 \times 10^{24} \text{ kg.}$$

$$\text{Mass of ball} = 0.1 \text{ kg}$$

$$\text{Mass of electron} = 9.1 \times 10^{-31} \text{ kg}$$

$$\text{Velocity of orbital motion of the earth} = 3 \times 10^4 \text{ m sec}^{-1}$$

$$\text{Velocity of the ball} = 100 \text{ m sec}^{-1}$$

$$\text{Velocity of the electron} = 1.0 \times 10^6 \text{ m sec}^{-1}$$

$$h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$$

In case of which of these three objects, will the wavelength be measurable ?

SOLUTION :

Formula used

$$\lambda = \frac{h}{m v}$$

(i) For earth

Quantities given

$$h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1} \quad m = 6.0 \times 10^{24} \text{ kg} \quad v = 3 \times 10^4 \text{ m sec}^{-1}$$

Substitution of values

$$\begin{aligned} \lambda &= \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}}{6.0 \times 10^{24} \text{ kg} \times 3 \times 10^4 \text{ m sec}^{-1}} \\ &= 3.66 \times 10^{-63} \text{ m} \end{aligned}$$

(ii) For ball

Quantities given

$$h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1} \quad m = 0.1 \text{ kg} \quad v = 100 \text{ m sec}^{-1}$$

Substitution of values

$$\begin{aligned} \lambda &= \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}}{0.1 \text{ kg} \times 100 \text{ m sec}^{-1}} \\ &= 6.6 \times 10^{-35} \text{ m} \end{aligned}$$

(ii) For electron

Quantities given

$$h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1} \quad m = 9.1 \times 10^{-31} \text{ kg} \quad v = 1.0 \times 10^6 \text{ m sec}^{-1}$$

Substitution of values

$$\begin{aligned} \lambda &= \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}}{(9.1 \times 10^{-31} \text{ kg}) \times (1.0 \times 10^6 \text{ m sec}^{-1})} \\ &= 7.25 \times 10^{-10} \text{ m} \end{aligned}$$

Thus the wavelength is measurable in case of electron only.

ADDITIONAL PRACTICE PROBLEMS

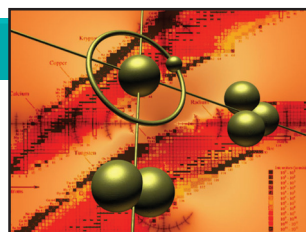
- Calculate the product of uncertainty of displacement and velocity of a moving electron.
($m = 9.1 \times 10^{-31}$ kg).
Answer. $5.80 \times 10^{-1} \text{ m}^2 \text{ sec}^{-1}$
- Calculate the momentum of a particle which has a de Broglie's wavelength of 0.1 nm.
Answer. $6.6 \times 10^{-24} \text{ kg m}^2 \text{ sec}^{-1}$
- The kinetic energy of an electron is 4.55×10^{-25} J. Calculate its wavelength ($h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$; mass of electron = 9.1×10^{-31} kg).
Answer. $7.25 \times 10^{-1} \text{ m}$
- The kinetic energy of a subatomic particle is 5.60×10^{-25} J. Calculate the frequency of the particle wave (Planck's Constant $h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$).
Answer. $1.696 \times 10^9 \text{ sec}^{-1}$
- Calculate the wavelength associated with an electron moving with a velocity of $1 \times 10^8 \text{ cm sec}^{-1}$. (mass of the electron = 9.1×10^{-28} g).
Answer. $7.28 \times 10^{-8} \text{ cm}$
- Calculate the de Broglie wavelength of an electron moving with a velocity of $6 \times 10^5 \text{ m sec}^{-1}$.
Answer. $1.456 \times 10^{-8} \text{ m}$
- Calculate the uncertainty in position of an electron if uncertainty in velocity is $5.7 \times 10^5 \text{ m sec}^{-1}$. ($h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$; mass of electron = 9×10^{-31} kg)
Answer. 10^{-10} m
- A body moving with a speed of 100 m sec^{-1} has a wavelength of $5 \times 10^{-36} \text{ m}$. Calculate the mass of the body. ($h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$).
Answer. 1.32 kg
- Calculate the uncertainty in momentum of an electron if uncertainty in its position is approximately 100 pm. ($5.0 \times 10^{-12} \text{ m}$).
Answer. $5.27 \times 10^{-25} \text{ kg m sec}^{-1}$
- Calculate the uncertainty in the velocity of a bullet of mass 10 g whose position at time t is known with uncertainty equal to $1.0 \times 10^{-5} \text{ m}$.
Answer. $5.628 \times 10^{-28} \text{ m sec}^{-1}$
- Calculate the uncertainty in the velocity of an electron if the uncertainty in position is $1 \times 10^{-10} \text{ m}$.
Answer. $5.76 \times 10^5 \text{ m sec}^{-1}$
- Calculate the uncertainty in the position of a particle when the uncertainty in the momentum is
(a) $1 \times 10^{-7} \text{ kg m sec}^{-1}$ and
(b) Zero
Answer. (a) $5.72 \times 10^{-28} \text{ m}$; (b) ∞
- Calculate the uncertainty in the velocity of a bullet weighing 10 g whose position is known with an accuracy of $\pm 0.1 \text{ nm}$.
Answer. $0.527 \times 10^{-27} \text{ m sec}^{-1}$
- Calculate the uncertainty in the velocity of a wagon of mass 2000 kg whose position is known with an accuracy of $\pm 10 \text{ m}$.
Answer. $5.25 \times 10^{-31} \text{ m sec}^{-1}$
- Calculate the product of uncertainty of displacement and velocity of a moving electron having a mass of $9.1 \times 10^{-31} \text{ kg}$ ($h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$).
Answer. $5.774 \times 10^{-5} \text{ m}^2 \text{ sec}^{-1}$
- A body moving with a speed of 100 m sec^{-1} has a wavelength of $5 \times 10^{-36} \text{ m}$. Calculate the mass of the body ($h = 6.6 \times 10^{-34} \text{ kg m}^2 \text{ sec}^{-1}$).
Answer. 1.32 kg

3

Isotopes, Isobars and Isotones

CHAPTER

KEY CONCEPTS AND EQUATIONS



ISOTOPES

The atoms of an element which have the same atomic number but different atomic masses or mass numbers are called Isotopes. They have the same number of protons (or electrons) and different number of neutrons. They have same position in the periodic table. Isotopes have similar chemical properties as they have the same electronic configuration. However, they differ in respect of physical properties which depend on their atomic masses. Examples of isotopes are

${}_1\text{H}^1$	${}_1\text{H}^2$	${}_1\text{H}^3$
Hydrogen	Deuterium	Tritium
${}_6\text{C}^{12}$	${}_6\text{C}^{13}$	${}_6\text{C}^{14}$
${}_8\text{O}^{16}$	${}_8\text{O}^{17}$	${}_8\text{O}^{18}$
${}_{92}\text{U}^{234}$	${}_{92}\text{U}^{235}$	${}_{92}\text{U}^{238}$

DETERMINING ATOMIC MASSES FROM ISOTOPIC MASSES AND FRACTIONAL ABUNDANCES

Multiply each of the isotopic masses by its fractional abundance and then add. For example to calculate the atomic mass of neon which has following isotopes in percentages as :

${}_{10}\text{Ne}^{20}$	90.92
${}_{10}\text{Ne}^{21}$	0.26
${}_{10}\text{Ne}^{22}$	8.82

Thus we have

$$\begin{array}{r}
 20 \times 0.9092 = 18.18 \\
 21 \times 0.0026 = 0.055 \\
 22 \times 0.0882 = 1.94 \\
 \hline
 20.175
 \end{array}$$

\therefore The atomic mass of Neon is 20.175

RATE OF DIFFUSION

The rate of diffusion is inversely proportional to the square root of its atomic mass (Graham's Law)
i.e.

$$\text{Rate of Diffusion} \propto \sqrt{\frac{1}{\text{Molecular mass}}}$$

Thus when a mixture of two isotopes is allowed to diffuse through a porous partition, **the lighter isotope passes through more rapidly than the heavier one.**

DETERMINING THE NUMBER OF ELECTRONS, PROTONS AND NEUTRONS

The isotopes of an element are characterised by different number of neutrons in the nucleus. The number of neutrons in the nucleus is equal to the difference between mass number (A) and the atomic number (Z) i.e.

$$\begin{aligned}\text{Number of neutrons} &= \text{Mass number} - \text{Atomic number} \\ &= A - Z\end{aligned}$$

WHAT ARE ISOBARS ?

The atoms which have the same mass number but different atomic numbers are called Isobars. They have different number of protons (or electrons) and neutrons but **the sum of protons and neutrons is the same.** Examples are :

	${}_{18}\text{Ar}^{40}$	${}_{19}\text{K}^{40}$	${}_{20}\text{Ca}^{40}$
No. of Protons	18	19	20
No. of Neutrons	22	21	20
Sum of Protons and Neutrons	40	40	40

WHAT ARE ISOTONES ?

Atoms which have different atomic numbers and different atomic masses but **the same number of neutrons** are called Isotones. Examples are :

	${}_6\text{C}^{14}$	${}_7\text{N}^{15}$	${}_8\text{O}^{16}$
No. of Protons	6	7	8
No. of Neutrons	8	8	8
Sum of Protons and Neutrons	14	15	16

Isotones have different physical and chemical properties.

COMPARISON OF ISOTOPES, ISOBARS AND ISOTONES

The comparison of Isotopes, Isobars and Isotones is given in the Table 3.1.

TABLE 3.1. COMPARISON OF ISOTOPES, ISOBARS AND ISOTONES				
Name	Mass number (A)	Atomic number (Z)	No. of neutrons (A - Z)	Examples
Isotopes	Different	Same	Different	${}_6\text{C}^{12}$, ${}_6\text{C}^{13}$, ${}_6\text{C}^{14}$
Isobars	Same	Different	Different	${}_{18}\text{Ar}^{40}$, ${}_{19}\text{K}^{40}$, ${}_{20}\text{Ca}^{40}$
Isotones	Different	Different	Same	${}_{14}\text{Si}^{30}$, ${}_{15}\text{P}^{31}$, ${}_{16}\text{S}^{32}$

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. Calculate the relative atomic mass of an element which consists of the following isotopes with the indicated relative abundance.

Isotope	Isotopic mass	Natural abundance
1	28	92.0
2	29	5.0
3	30	3.0

SOLUTION :

The atomic mass of an ordinary isotopic mixture is the average of the determined atomic masses of individual isotopes. Thus

$$\begin{array}{rcl}
 28 \times 0.92 & = & 25.76 \\
 29 \times 0.05 & = & 1.45 \\
 30 \times 0.03 & = & 0.90 \\
 \text{Total} & & \underline{28.11}
 \end{array}$$

Thus the atomic mass is 28.11 amu

SOLVED PROBLEM 2. Chromium, Cr, has following isotopic masses and fractional abundances :

Mass Number	Mass (amu)	Fractional abundance
50	49.9461	0.0435
52	51.9405	0.8379
53	52.9407	0.0950
54	53.9389	0.0236

SOLUTION :

Multiplying each isotope by its fractional abundance, we have

$$\begin{array}{rcl}
 49.9461 \text{ amu} \times 0.0435 & = & 2.17 \text{ amu} \\
 51.9405 \text{ amu} \times 0.8379 & = & 43.52 \text{ amu} \\
 52.9407 \text{ amu} \times 0.0950 & = & 5.03 \text{ amu} \\
 53.9389 \text{ amu} \times 0.0236 & = & 1.27 \text{ amu} \\
 \text{Total} & & \underline{51.99 \text{ amu}}
 \end{array}$$

Thus the atomic mass of chromium is 51.99 amu

SOLVED PROBLEM 3. Calculate the atomic mass of boron, B, from the following data :

Isotope	Atomic mass (amu)	Fractional abundance
${}^5_5\text{B}^{10}$	10.013	0.1978
${}^5_5\text{B}^{11}$	11.009	0.8022

SOLUTION :

Multiplying each isotope by its fractional abundance, we have

$$\begin{array}{rcl}
 10.013 \text{ amu} \times 0.1978 & = & 1.9806 \text{ amu} \\
 11.009 \text{ amu} \times 0.8022 & = & 8.8314 \text{ amu} \\
 \text{Total} & & \underline{10.8120 \text{ amu}}
 \end{array}$$

Thus the atomic mass of Boron is 10.8120 amu

SOLVED PROBLEM 3. Naturally occurring boron consists of two isotopes whose atomic masses are 10.01 and 11.01. The atomic mass of naturally occurring boron is 10.81. Calculate the percentage of each isotope in natural boron.

SOLUTION :

Let the percentage of isotope with atomic mass 10.01 be A .

\therefore the percentage of isotope with atomic mass 11.01 = $100 - A$

$$\text{Now the atomic mass} = \frac{A \times 10.01 + (100 - A) \times 11.01}{100}$$

$$10.81 = \frac{10.01A + 1101 - 11.01A}{100}$$

$$\text{or} \quad 11.01A - 10.01A = 1101 - 1081$$

$$\text{or} \quad A = 20$$

Hence the percentage of isotope with atomic mass

$$10.01 = 20$$

and the percentage of isotope with atomic mass

$$11.01 = 80$$

ADDITIONAL PRACTICE PROBLEMS

- Magnesium has naturally occurring isotopes with the following masses and abundances.

Isotope	Atomic mass (amu)	Fractional abundance
$^{24}_{12}\text{Mg}$	23.985	0.7870
$^{25}_{12}\text{Mg}$	24.986	0.1013
$^{26}_{12}\text{Mg}$	25.983	0.1117

Calculate the atomic mass of magnesium.

Answer. 24.31 amu

- Silver has two naturally occurring isotopes with atomic masses 106.91 and 108.90 amu. The atomic mass of silver is 107.87 amu. Calculate the fractional abundances for these two isotopes.

Answer. 0.518 ; 0.482

- Calculate the fractional abundances for the two naturally occurring isotopes of copper. The masses of the isotopes are 62.9298 and 64.9278 amu. The atomic mass of copper is 63.546 amu.

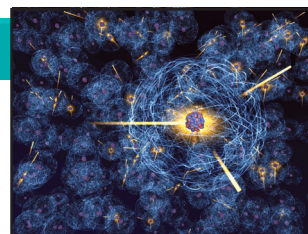
Answer. 0.692 ; 0.308]

4

Nuclear Chemistry

CHAPTER

KEY CONCEPTS AND EQUATIONS



RADIOACTIVITY AND TYPES OF RADIATIONS

The disintegration or decay of unstable atoms accompanied by emission of radiation is called **Radioactivity**. The substances having this property are called **Radioactive substances**. The radioactive emissions are of three types - α , β , or γ radiations as shown in Fig. 4.1.

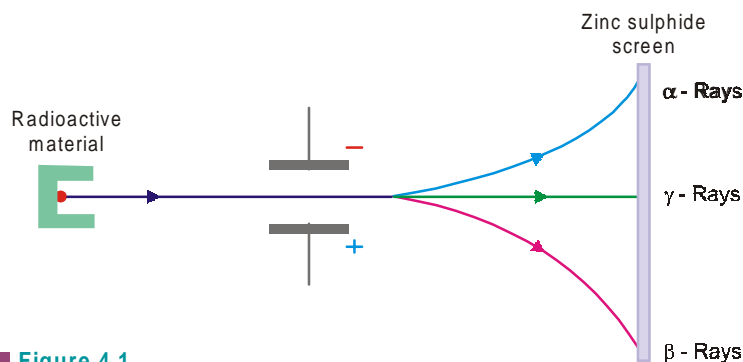


Figure 4.1
Detection of α , β and γ -Rays.

The charge and mass of α , β and γ - particles are given in Table 4.1

TABLE 4.1 CHARGE AND MASS OF α , β AND γ -EMISSIONS			
Particle	Charge	Mass	Representation
α	2	4	${}_2\text{He}^4$ or ${}_2\alpha^4$
β	-1	0	${}_{-1}\text{e}^0$ or ${}_{-1}\beta^0$
γ	0	0	${}_0\gamma^0$

RATE OF RADIOACTIVE DECAY (No. of disintegrations per unit time)

The rate of decay is characteristic of an isotope and depends only on the number of atoms present. It is given by

$$-\frac{dN}{dt} = \lambda N$$

where λ is disintegration constant and N is number of atoms present.

On integration we have

$$\lambda = \frac{2.303}{t} \log \frac{N^0}{N} \quad \dots(i)$$

where N^0 is the number of atoms at $t = 0$

Radioactive disintegration follows the first order kinetics and the equation

$$\lambda = \frac{2.303}{t} \log \frac{a}{a-x} \quad \dots(ii)$$

is also applicable.

HALF LIFE PERIOD

The half life period of a radioactive isotope is the time required for one half of the isotope to decay. It is represented by $t_{1/2}$ or $t_{0.5}$

$$\text{When } t = t_{1/2} \quad N = \frac{N^0}{2}$$

Putting in equation (i) we have

$$t_{1/2} = \frac{2.303}{\lambda} \log 2 = \frac{0.693}{\lambda}$$

It is independent of initial concentration of radioactive substance.

AVERAGE LIFE

The average life of a radioactive substance is the reciprocal of disintegration constant *i.e.*,

$$\lambda' = \frac{1}{\lambda} = \frac{t_{1/2}}{0.693} = 1.44 \times t_{1/2}$$

UNITS OF RADIOACTIVITY

The unit of radioactivity is disintegration per second (dps). It is also expressed in curie or rutherford or becquerel. These are related to dps as follows :

$$\begin{aligned} 1 \text{ curie} &= 3.7 \times 10^{10} \text{ dps} \\ 1 \text{ rutherford} &= 1 \times 10^6 \text{ dps} \\ 1 \text{ becquerel} &= 1 \text{ dps} \end{aligned}$$

RADIOACTIVE EQUILIBRIUM

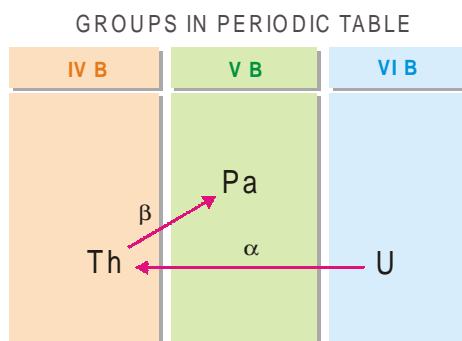
Let a radioactive substance A decay to give another radioactive substance B which decays to form the substance C. If λ_A and λ_B are their decay constants then we have



$$\frac{N_A}{N_B} = \frac{\lambda_B}{\lambda_A} = \frac{(t_{1/2})_B}{(t_{1/2})_A}$$

GROUP DISPLACEMENT LAW

In an α emission the parent element is displaced to a group **two** places to left and in β emission it will be displaced to a group **one** place to the right in the periodic table as illustrated in Fig.4.2. This is called Group Displacement Law. It was first stated by Fajans and Soddy (1913) and is often named as Fajans-Soddy Group Displacement law.



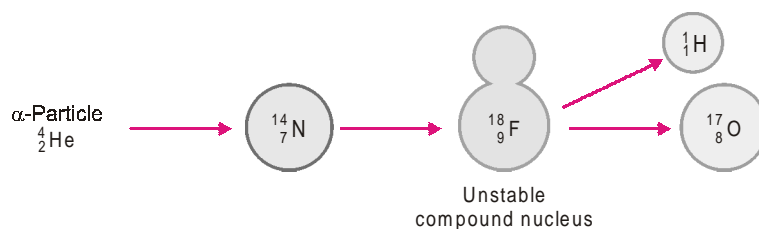
■ **Figure 4.2**
Illustration of Group Displacement Law.

NUCLEAR REACTIONS

A nuclear reaction is one which proceeds with a change in the composition of the nucleus so as to produce an atom of a new element. The conversion of one element to another by a nuclear change is called transmutation.

NUCLEAR FISSION REACTIONS

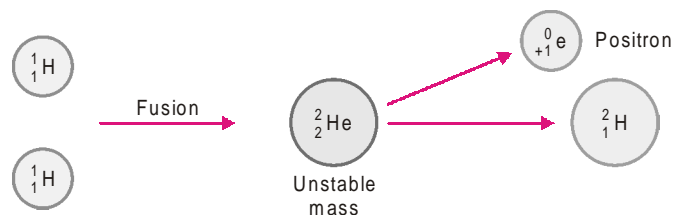
In these reactions an atomic nucleus is broken or fissioned into two or more fragments. For example, ${}_{7}^{14}\text{N}$ when struck by an α - particle first forms an intermediate unstable compound nucleus, ${}_{9}^{18}\text{F}$, which at once cleaves to form stable ${}_{8}^{17}\text{O}$ and ${}_{1}^{1}\text{H}$.



■ **Figure 4.3**
Mechanism of a Nuclear fission reaction.

NUCLEAR FUSION REACTIONS

These reactions take place by combination or fusion of two small nuclei into a larger nucleus. For example two hydrogen nuclei, ${}_{1}^{1}\text{H}$, fuse to produce a deuterium nucleus, ${}_{1}^{2}\text{H}$ as shown in Fig. 4.4.



■ **Figure 4.4**
Mechanism of a Nuclear fission reaction.

MASS-ENERGY EQUIVALENCE

Mass and energy are equivalent and are related to each other by the equation.

$$E = mc^2$$

where c is the speed of light, m sec^{-1} .

This equation is known as Einstein equation.

MASS DEFECT AND BINDING ENERGY

The difference between the experimental and calculated mass of the nucleus is called the mass defect.

Mass defect = Experimental mass of the nucleus – (mass of protons + electrons + neutrons).

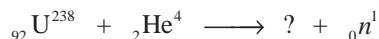
It is equal to the total nucleon mass minus the nuclear mass. This loss of mass is converted into energy which stabilizes the nucleus. This energy is known as binding energy. It is also equal to the energy needed to break a nucleus into its individual protons and neutrons. Einstein equation is used to calculate the binding energy. With mass defect of 1 amu 931.5 MeV of energy is produced *i.e.*

$$1 \text{ amu} = 931.5 \text{ MeV}$$

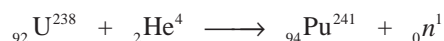
To compare the stabilities of various nuclei, the binding energy per nucleon is compared.

BALANCING OF NUCLEAR EQUATIONS

The equations involving the nuclei of the reactants and products are called nuclear equations. The nuclear reactions occur by redistribution of protons and neutrons present in the reactants so as to form the products. Thus the total number of protons and neutrons in the reactants and products is the same. For example in the nuclear equation



the atomic number of missing atom is 94 and its mass no. is $238 + 4 - 1 = 241$. Hence the atom is ${}_{94}\text{Pu}^{241}$. The balanced equation becomes.



ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. It is found that a sample of radioactive matter is half integrated in 18 hours. How much of it will remain after 42.5 hours ?

SOLUTION :

(i) To calculate disintegration constant

Formula used $\lambda = \frac{0.693}{t_{1/2}}$

Quantities given $t_{1/2} = 18 \text{ hr}$

Substitution of values $\lambda = \frac{0.693}{18 \text{ hr}} = 0.0385 \text{ hr}^{-1}$

(ii) To calculate the amount of sample left after 42.5 hours

Formula used

$$\lambda = \frac{1}{t} \log \frac{a}{a-x}$$

Quantities given

$$\lambda = 0.0385 \text{ hr}^{-1} \quad t = 42.5 \text{ hours} \quad a = 100 \quad a-x = 100-x$$

Substitution of values

$$0.0385 \text{ hr}^{-1} = \frac{1}{42.5 \text{ hr}} \log \frac{100}{100-x}$$

$$\text{or} \quad 1.63625 = \log \frac{100}{100-x}$$

$$\text{or} \quad \frac{100}{100-x} = \text{Antilog } 1.63625$$

$$= 5.13$$

$$\text{or} \quad 100 = 5.13 \times (100-x)$$

$$100 = 513 - 5.13x$$

$$\text{or} \quad x = \frac{413}{5.13}$$

$$= 80.51$$

$$\therefore \text{Amount left} = 100 - 80.51$$

$$= \mathbf{19.49\%}$$

SOLVED PROBLEM 2. Radium has atomic mass 226 and a half life of 1600 years. Calculate the number of disintegration produced per second from one gram of radium.

SOLUTION :

(i) To calculate the disintegration constant

Formula used $\lambda = \frac{0.693}{t_{1/2}}$

Quantities given

$$t_{1/2} = 1600 \text{ years} = 1600 \times 365 \times 24 \times 60 \times 60 \text{ sec} \\ = 5.04576 \times 10^{10} \text{ sec}$$

Substitution of values

$$\therefore \lambda = \frac{0.693}{5.04576 \times 10^{10} \text{ sec}} \\ = 0.1373 \times 10^{-10} \text{ sec}^{-1}$$

(ii) To calculate the rate of disintegration

Formula used $-\frac{dN}{dt} = \lambda \times N$

Quantities given $\lambda = 0.1373 \times 10^{-10} \text{ sec}^{-1}$

No. of nuclei of Ra^{226} in 1g, $N = \frac{\text{Avogadro's No.}}{226}$

$$= \frac{6.023 \times 10^{23}}{226} \\ = 0.0266 \times 10^{-23} \text{ atoms}$$

Substitution of values

Rate of disintegration, $-\frac{dN}{dt} = 0.1373 \times 10^{-10} \text{ sec}^{-1} \times 0.0266 \times 10^{-23} \text{ atoms}$

$$= 0.003652 \times 10^{-13} \text{ atom sec}^{-1} \\ = \mathbf{3.652 \times 10^{16} \text{ atom sec}^{-1}}$$

SOLVED PROBLEM 3. The activity of a radioactive isotope reduces by 25% after 100 minutes. Calculate the decay constant and half life period.

SOLUTION :

(i) To calculate decay constant

Formula used $\lambda = \frac{2.303}{t} \log \frac{a}{a-x}$

Quantities given

$$t = 100 \text{ min}$$

$$a = 100$$

$$a-x = 25$$

Substitution of values

$$\lambda = \frac{2.303}{100 \text{ min}} \log \frac{100}{25} \\ = 0.02303 \text{ min}^{-1} \times \log 4 \\ = 0.02303 \text{ min}^{-1} \times 0.6021 \\ = \mathbf{0.01387 \text{ min}^{-1}}$$

(ii) To calculate Half Life period

$$\begin{aligned} \text{Formula used} \quad t_{1/2} &= \frac{0.693}{\lambda} \\ \therefore t_{1/2} &= \frac{0.693}{0.01386 \text{ min}^{-1}} \\ &= \mathbf{49.96 \text{ min}} \end{aligned}$$

SOLVED PROBLEM 4. Calculate the number of α and β particles emitted in the conversion of thorium ${}_{90}\text{Th}^{232}$ to ${}_{82}\text{Pb}^{208}$.

SOLUTION :

Let x and y be the number of α and β particles emitted during the change



Comparing the mass numbers, we have

$$232 = 208 + 4x + y \times 0$$

$$\text{or} \quad 4x = 24$$

$$\text{or} \quad x = \mathbf{6}$$

Now comparing the atomic numbers, we have

$$90 = 82 + 2x - 1y$$

$$\text{or} \quad 90 = 82 + 2 \times 6 - y \quad (\because x=6)$$

$$\text{or} \quad y = 94 - 90$$

$$= \mathbf{4}$$

SOLVED PROBLEM 5. Half life period of thorium is 24.5 minutes. How much thorium would be left after 30 minutes if the initial amount of thorium is one gram ?

SOLUTION :**(i) To calculate the disintegration constant**

Formula used

$$\lambda = \frac{0.693}{t_{1/2}}$$

Quantities given

$$t_{1/2} = 24.5 \text{ min}$$

Substitution of values

$$\begin{aligned} \lambda &= \frac{0.693}{24.5 \text{ min}} \\ &= \mathbf{0.02828 \text{ min}^{-1}} \end{aligned}$$

(ii) To calculate the amount of Thorium left

Formula used

$$\lambda = \frac{1}{t} \log \frac{a}{a-x}$$

Quantities given

$$\lambda = 0.02828 \text{ min}^{-1}$$

$$t = 30 \text{ minutes}$$

$$a = 1 \text{ g}$$

$$a-x = 1-x \text{ g}$$

Substitution of values

$$0.02828 \text{ min}^{-1} = \frac{1}{30 \text{ min}} \log \frac{1}{1-x}$$

$$\begin{aligned} \text{or} \quad \log \frac{1}{1-x} &= 30 \times 0.02828 \\ &= 0.8484 \end{aligned}$$

$$\begin{aligned} \text{or} \quad \frac{1}{1-x} &= \text{Antilog } 0.8484 \\ &= 2.3359 \end{aligned}$$

$$\begin{aligned} \text{or} \quad 1 &= (1-x) 2.3359 \\ 1 &= 2.3359 - 2.3359x \end{aligned}$$

$$\begin{aligned} \text{or} \quad x &= \frac{2.3359 - 1}{2.3359} \\ &= 0.572 \text{ g} \end{aligned}$$

$$\begin{aligned} \therefore \text{Amount left} &= 1 - x \\ &= 1 - 0.572 \text{ g} \\ &= \mathbf{0.428 \text{ g}} \end{aligned}$$

SOLVED PROBLEM 6. How many α and β particles will be emitted by an element ${}_{84}\text{A}^{218}$ is changing to a stable isotope of ${}_{82}\text{B}^{206}$?

SOLUTION :

Let x and y be the number of α and β particles respectively emitted during the change



Comparing the mass number

$$\begin{aligned} 218 &= 206 + 4x + 0y \\ \text{or} \quad 4x &= 12 \\ \text{or} \quad x &= \mathbf{3} \end{aligned}$$

Now comparing the atomic numbers

$$\begin{aligned} 84 &= 82 + 2x - y \\ 84 &= 82 + 2 \times 3 - y & [\because x = 3] \\ \text{or} \quad y &= \mathbf{4} \end{aligned}$$

SOLVED PROBLEM 7. Calculate the decay constant for Ag^{108} , if its half life is 2.31 minutes.

SOLUTION :**Formula used**

$$\lambda = \frac{0.693}{t_{1/2}}$$

Quantities given

$$t_{1/2} = 2.31 \text{ minutes}$$

Substitution of values

$$\begin{aligned} \lambda &= \frac{0.693}{2.31 \text{ min}} \\ &= \mathbf{0.3 \text{ min}^{-1}} \end{aligned}$$

SOLVED PROBLEM 8. A radioactive isotope has half life period of 20 days. What is the amount of the isotope left over after 40 days if the initial concentration is 5 g ?

SOLUTION :

(i) To calculate the decay constant

Formula used

$$\lambda = \frac{0.693}{t_{1/2}}$$

Quantities given

$$t_{1/2} = 20 \text{ days}$$

Substitution of values

$$\begin{aligned}\lambda &= \frac{0.693}{20 \text{ days}} \\ &= \mathbf{0.03465 \text{ day}^{-1}}\end{aligned}$$

(ii) To calculate amount of radioactive isotope

Formula used

$$\lambda = \frac{1}{t} \log \frac{a}{a-x}$$

Quantities given

$$t = 40 \text{ days}$$

$$a = 5 \text{ g}$$

$$a-x = 5-x \text{ g}$$

Substitution of values

$$0.03465 \text{ day}^{-1} = \frac{1}{40 \text{ days}} \log \frac{5}{5-x}$$

$$\text{or} \quad \log \frac{5}{5-x} = 1.386$$

$$\text{or} \quad \frac{5}{5-x} = \text{Antilog } 1.386$$

$$= 3.9988$$

$$5 = (5-x) \times 3.9988$$

$$\text{or} \quad x = 3.75 \text{ g}$$

$$\begin{aligned}\therefore \text{Amount left} &= \text{Initial concentration} - \text{Amount used} \\ &= 5 - 3.75 \text{ g} \\ &= \mathbf{1.25 \text{ g}}\end{aligned}$$

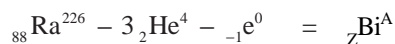
SOLVED PROBLEM 9. Calculate the mass number, atomic number and group in the periodic table for Bi in the following disintegration series.



(Ra : Mass No. 226, at. no. 88, group no. II A)

SOLUTION :

We can write



Comparing the mass numbers

$$226 - 3 \times 4 - 0 = A$$

$$\text{or} \quad A = \mathbf{214}$$

Comparing the atomic numbers

$$88 - 3 \times 2 - 1 \times (-1) = Z$$

$$\text{or} \quad Z = \mathbf{83}$$

$$\text{Group} = \mathbf{VA}$$

SOLVED PROBLEM 10. The half life of Th^{233} is 1.4×10^{10} years. Calculate the disintegration constant.

SOLUTION :

Formula used

$$\lambda = \frac{0.693}{t_{1/2}}$$

Quantities given

$$t_{1/2} = 1.4 \times 10^{10} \text{ years}$$

Substitution of values

$$\begin{aligned}\lambda &= \frac{0.693}{1.4 \times 10^{10} \text{ years}} \\ &= 0.495 \times 10^{10} \text{ year}^{-1} \\ &= \mathbf{4.95 \times 10^{-11} \text{ year}^{-1}}\end{aligned}$$

SOLVED PROBLEM 11. A radioactive substance having half life of 3.8 days, emitted initially alpha particles per second. In what time will its rate of emission reduces to alpha particles per second ?

SOLUTION :

(i) To calculate disintegration constant

Formula used

$$\lambda = \frac{0.693}{t_{1/2}}$$

Quantities given

$$t_{1/2} = 3.8 \text{ days}$$

Substitution of values

$$\begin{aligned}\lambda &= \frac{0.693}{3.8 \text{ days}} \\ &= \mathbf{0.1824 \text{ day}^{-1}}\end{aligned}$$

(ii) To calculate the time t

Formula used

$$\lambda = \frac{2.303}{t} \log \frac{N^0}{N}$$

or

$$t = \frac{2.303}{\lambda} \log \frac{N^0}{N}$$

Quantities given

$$\lambda = 0.1824 \text{ days}^{-1}$$

$$N^0 = 7 \times 10^4 \text{ dps}$$

$$N = 2 \times 10^4 \text{ dps}$$

Substitution of values

$$\begin{aligned}t &= \frac{2.303}{0.1824 \text{ day}^{-1}} \log \frac{7 \times 10^4 \text{ dps}}{2 \times 10^4 \text{ dps}} \\ &= \frac{2.303}{0.1824 \text{ day}^{-1}} \log 3.5 \\ &= \frac{2.303}{0.1824 \text{ day}^{-1}} \times 0.5440 \\ &= \mathbf{6.872 \text{ days}}\end{aligned}$$

SOLVED PROBLEM 12. A freshly cut piece of plant gives 20.4 counts per minute per gram. A piece of wood antique gives 12.18 counts per minute per gram. What is the age in years of antique ? It is assumed that the radioactivity is entirely due to C^{14} . The half life period of C^{14} is 5760 years.

SOLUTION :

(i) To calculate the disintegration constant

Formula used

$$\lambda = \frac{0.693}{t_{1/2}}$$

Quantities given

$$t_{1/2} = 5760 \text{ years}$$

Substitution of values

$$\begin{aligned}\lambda &= \frac{0.693}{5790 \text{ years}} \\ &= 1.203 \times 10^{-4} \text{ year}^{-1}\end{aligned}$$

(ii) To calculate the age of antique

Formula used

$$\lambda = \frac{2.303}{t} \log \frac{N^0}{N}$$

or

$$t = \frac{2.303}{\lambda} \log \frac{N^0}{N}$$

Quantities given

$$\lambda = 2.303 \times 10^{-4} \text{ year}^{-1} \quad N^0 = 20.4 \text{ counts per minutes per g}$$

$$N = 12.18 \text{ counts per minutes per g}$$

Substitution of values

$$\begin{aligned}t &= \frac{2.303}{2.303 \times 10^{-4} \text{ year}^{-1}} \log \frac{20.4}{12.18} \\ &= \frac{2.303}{2.303 \times 10^{-4} \text{ year}^{-1}} \log 1.6749 \\ &= \frac{2.303}{2.303 \times 10^{-4} \text{ year}^{-1}} \times 0.2339 \\ &= 4287.43 \text{ years}\end{aligned}$$

SOLVED PROBLEM 13. 2 g of a radioactive element degraded to 0.5 g in 60 hours. In what time will it be reduced 10% of its original amount ?

SOLUTION :

(i) To calculate the disintegration constant

Formula used

$$\lambda = \frac{2.303}{t} \log \frac{a}{a-x}$$

Quantities given

$$t = 60 \text{ hours}$$

$$a = 2 \text{ g}$$

$$a-x = 0.5 \text{ g}$$

Substitution of values

$$\begin{aligned}\lambda &= \frac{2.303}{60 \text{ hours}} \times \log \frac{2}{0.5} \\ &= \frac{2.303}{60 \text{ hours}} \times \log 4\end{aligned}$$

$$\begin{aligned}
 &= \frac{2.303}{60 \text{ hours}} \times 0.6021 \\
 &= \mathbf{2.311 \times 10^{-2} \text{ hour}^{-1}}
 \end{aligned}$$

(ii) To calculate the time t

Formula used

$$\lambda = \frac{2.303}{t} \log \frac{a}{a-x}$$

or

$$t = \frac{2.303}{\lambda} \log \frac{a}{a-x}$$

Quantities given

$$\lambda = 2.311 \times 10^{-2} \text{ hour}^{-1} \quad a = 2 \text{ g} \quad a-x = 90\% \text{ of } a = 1.8 \text{ g}$$

Substitution of values

$$\begin{aligned}
 t &= \frac{2.303}{2.311 \times 10^{-2} \text{ hour}^{-1}} \times \log \frac{2}{1.8} \\
 &= \frac{2.303}{2.311 \times 10^{-2} \text{ hour}^{-1}} \times \log 1.11 \\
 &= \frac{2.303}{2.311 \times 10^{-2} \text{ hour}^{-1}} \times 0.0453 \\
 &= \mathbf{4.51 \text{ hours}}
 \end{aligned}$$

SOLVED PROBLEM 14. A radioactive isotope has half life of 20 days. What is the amount of isotope left over after 40 days if the initial amount is 5 g ?

SOLUTION :

(i) To calculate the disintegration constant

Formula used

$$\lambda = \frac{0.693}{t_{1/2}}$$

Quantity given

$$t_{1/2} = 20 \text{ days}$$

Substitution of values

$$\begin{aligned}
 \lambda &= \frac{0.693}{20 \text{ days}} \\
 &= \mathbf{0.03465 \text{ day}^{-1}}
 \end{aligned}$$

(ii) To calculate the amount decayed, x

Formula used

$$\lambda = \frac{2.303}{t} \log \frac{a}{a-x}$$

Quantities given

$$t = 40 \text{ days}$$

$$\lambda = 0.03465 \text{ day}^{-1}$$

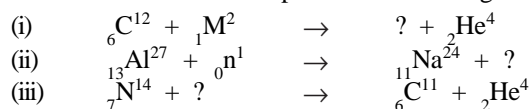
$$a = 5 \text{ g}$$

Substitution of values

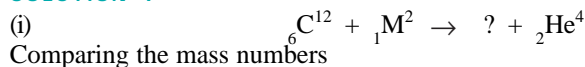
$$\begin{aligned}
 0.03465 \text{ day}^{-1} &= \frac{2.303}{40 \text{ days}} \log \frac{5}{5-x} \\
 \log \frac{5}{5-x} &= \frac{0.03465 \text{ day}^{-1} \times 40 \text{ days}}{2.303} \\
 &= 0.6018 \\
 \text{or} \quad \frac{5}{5-x} &= \text{Antilog } 0.6018 \\
 &= 3.9978 \\
 \text{or} \quad 5 &= (5-x) \times 3.9978
 \end{aligned}$$

$$\begin{aligned}
 5 &= 5 \times 3.9978 - 3.9978x \\
 \text{or} \quad x &= \frac{19.989 - 5}{3.9978} \\
 &= 3.75 \text{ g} \\
 \therefore \quad \text{Amount left} &= 5 - 3.75 \text{ g} \\
 &= \mathbf{1.25 \text{ g}}
 \end{aligned}$$

SOLVED PROBLEM 15. Complete the following nuclear reactions :



SOLUTION :



$$12 + 2 = x + 4$$

$$\text{or} \quad x = 10$$

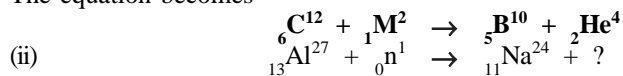
Comparing the atomic numbers

$$6 + 1 = y + 2$$

$$\text{or} \quad y = 5$$

Therefore the missing particle is ${}_5\text{B}^{10}$

The equation becomes



Comparing mass numbers

$$27 + 1 = 24 + x$$

$$\text{or} \quad x = 4$$

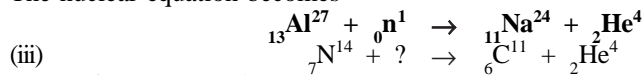
Comparing atomic numbers

$$13 + 0 = 11 + y$$

$$\text{or} \quad y = 2$$

\therefore the missing particle is ${}_2\text{He}^4$

The nuclear equation becomes



Comparing mass numbers

$$14 + x = 11 + 4$$

$$\text{or} \quad x = 1$$

Comparing atomic numbers

$$7 + y = 6 + 2$$

$$\text{or} \quad y = 1$$

\therefore the missing particle is ${}_1\text{H}^1$

The nuclear equation becomes



SOLVED PROBLEM 16. Calculate the rate of disintegration of one gram of Th^{232} if its decay constant is .

SOLUTION :

(i) To calculate the number of nuclei in 1 g of Th

$$\text{No. of nuclei in 1 g of Th} = \frac{\text{Avogadro's No.}}{\text{at. mass}}$$

$$= \frac{6.02 \times 10^{23}}{232}$$

$$= 2.5948 \times 10^{21} \text{ atoms}$$

(ii) To calculate the rate of disintegration

Formula used

$$\frac{dN}{dt} = \lambda \times N$$

Quantities given

$$\lambda = 1.58 \times 10^{-18} \text{ sec}^{-1}$$

$$N = 2.5948 \times 10^{21} \text{ atoms}$$

Substitution of values

$$\frac{dN}{dt} = 1.58 \times 10^{-18} \text{ sec}^{-1} \times 2.5948 \times 10^{21} \text{ atoms}$$

$$= 4.099 \times 10^3 \text{ dps}$$

SOLVED PROBLEM 17. Calculate the mass defect, binding energy and the binding energy per nucleon of ${}^4_2\text{He}$ which has an isotopic mass of 4.0026 amu (${}_1^1\text{H} = 1.0081 \text{ amu}$; ${}_0^1\text{H} = 1.0089 \text{ amu}$).

SOLUTION :

$$\begin{aligned} \text{Mass of 2 protons + mass of 2 electron} &= 2 \times \text{mass of } {}_1^1\text{H} \\ &= 2 \times 1.0081 \text{ amu} \\ &= 2.0162 \text{ amu} \end{aligned}$$

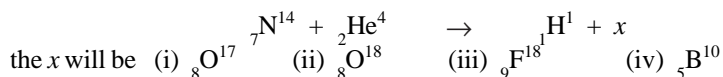
$$\begin{aligned} \text{and mass of 2 neutrons} &= 2 \times 1.0089 \text{ amu} \\ &= 2.0178 \text{ amu} \\ \text{mass of He atom} &= 2.0162 + 2.0178 \text{ amu} \\ &= 4.034 \text{ amu} \end{aligned}$$

$$\begin{aligned} \text{But Actual mass of He atom} &= 4.0026 \text{ amu} \\ \text{Mass defect (i.e. loss of mass)} &= 4.034 \text{ amu} - 4.0026 \text{ amu} \\ &= \mathbf{0.0314 \text{ amu}} \end{aligned}$$

$$\begin{aligned} \text{Binding Energy} &= \text{Mass defect} \times 931.5 \text{ MeV} \\ &= 0.0314 \times 931.5 \text{ MeV} \\ &= \mathbf{29.249 \text{ MeV}} \end{aligned}$$

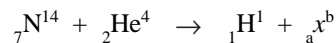
$$\begin{aligned} \text{and Binding energy per nucleon} &= \frac{29.249 \text{ MeV}}{4} \\ &= \mathbf{7.3122 \text{ MeV}} \end{aligned}$$

SOLVED PROBLEM 18. In the nuclear reaction



SOLUTION :

The nuclear reaction is



Comparing the mass numbers

$$\begin{aligned} 14 + 4 &= 1 + b \\ \text{or } b &= 17 \end{aligned}$$

Comparing the atomic numbers

$$\begin{aligned} 7 + 2 &= 1 + a \\ \text{or } a &= 8 \end{aligned}$$

$$\therefore x \text{ will be } {}_8^{17}\text{O}$$

SOLVED PROBLEM 19. The activity of a radioactive sample falls to 85% of the initial value in four years. What is the half life of the sample ? Calculate the time by which activity will fall by 85%.

SOLUTION :

(i) To calculate the disintegration constant

Formula used

$$\lambda = \frac{2.303}{t} \log \frac{a}{a-x}$$

Quantities given

$$t = 4 \text{ years}$$

$$a = 100 \quad a-x = 85$$

Substitution of values

$$\begin{aligned} \lambda &= \frac{2.303}{4 \text{ years}} \log \frac{100}{85} \\ &= \frac{2.303}{4 \text{ years}} \log 1.1765 \\ &= \frac{2.303}{4 \text{ years}} \times 0.0705 \\ &= 4.059 \times 10^{-2} \text{ year}^{-1} \end{aligned}$$

(ii) To calculate half life period

Formula used

$$\begin{aligned} t_{1/2} &= \frac{0.693}{\lambda} \\ \therefore \lambda &= \frac{0.693}{4.059 \times 10^{-2} \text{ year}^{-1}} \\ &= 17.07 \text{ years} \end{aligned}$$

(iii) To calculate the time

Formula used

$$\lambda = \frac{2.303}{t} \log \frac{a}{a-x}$$

or

$$t = \frac{2.303}{\lambda} \log \frac{a}{a-x}$$

Quantities given

$$\lambda = 4.059 \times 10^{-2} \text{ year}^{-1}$$

$$a = 100 \quad a-x = 15$$

Substitution of values

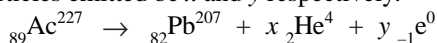
$$\begin{aligned} t &= \frac{2.303}{4.059 \times 10^{-2} \text{ year}^{-1}} \log \frac{100}{15} \\ &= \frac{2.303}{4.059 \times 10^{-2} \text{ year}^{-1}} \times \log 6.66 \\ &= 46.69 \text{ years} \end{aligned}$$

SOLVED PROBLEM 20. The mass number and atomic number of a radioactive element Actinium are 227 and 89 respectively. Calculate the number of α and β particles emitted, if the mass number and atomic number of the new element lead are 207 and 82 respectively.

SOLUTION :

Let the number of α and β particles emitted be x and y respectively.

Let the number of α and β particles emitted be x and y respectively.



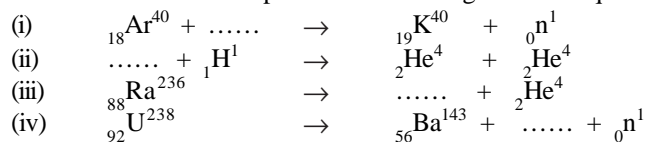
Comparing the mass numbers, we have

$$\begin{aligned}
 227 &= 207 + x \times 4 + y \times 0 \\
 \text{or } 4x &= 20 \\
 x &= 5
 \end{aligned}$$

Now comparing the atomic numbers, we have

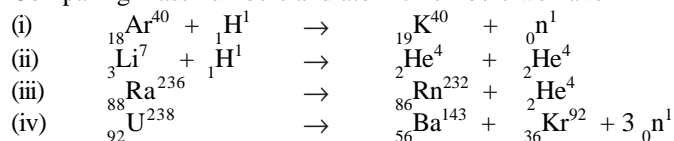
$$\begin{aligned}
 89 &= 82 + 2x + y(-1) \\
 89 - 82 &= 2x - y \\
 \text{or } 7 &= 2 \times 5 - y \\
 \text{or } y &= 3 \quad (\because x = 5)
 \end{aligned}$$

SOLVED PROBLEM 21. Complete the following nuclear equations :



SOLUTION :

Comparing mass numbers and atomic numbers we have



SOLVED PROBLEM 22. Calculate the age of the tooth in which C^{14} activity is 20% of the activity found at the present time ($t_{1/2}$ for C^{14} = 5580 years).

SOLUTION :

(i) To calculate the disintegration constant

Formula used

$$\lambda = \frac{0.693}{t_{1/2}}$$

Quantity given

$$t_{1/2} = 5580 \text{ years}$$

Substitution of values

$$\begin{aligned}
 \lambda &= \frac{0.693}{5580 \text{ years}} \\
 &= 1.2419 \times 10^{-4} \text{ year}^{-1}
 \end{aligned}$$

(ii) To calculate the time

Formula used

$$\begin{aligned}
 \lambda &= \frac{2.303}{t} \log \frac{N^0}{N} \\
 \text{or } t &= \frac{2.303}{\lambda} \log \frac{N^0}{N}
 \end{aligned}$$

or

Quantities given

$$\lambda = 1.1785 \times 10^{-4} \text{ year}^{-1}$$

$$N^0 = 100$$

$$N = 20$$

Substitution of values

$$\begin{aligned}
 t &= \frac{2.303}{1.2419 \times 10^{-4} \text{ year}^{-1}} \log \frac{100}{20} \\
 &= \frac{2.303}{1.2419 \times 10^{-4} \text{ year}^{-1}} \log 5 \\
 &= \frac{2.303 \times 0.6990}{1.2419 \times 10^{-4} \text{ year}^{-1}} \\
 &= \mathbf{12962 \text{ years}}
 \end{aligned}$$

SOLVED PROBLEM 23. An old wooden article shows 2.0 counts per minute per gram. A fresh sample of wood shows 15.2 counts per minute per gram. Calculate the age of the wooden article ($t_{1/2}$ for $C^{14} = 5760$ years)..

SOLUTION :

(i) To calculate the disintegration constant

Formula used

$$\lambda = \frac{0.693}{t_{1/2}}$$

Quantity given

$$t_{1/2} = 5760 \text{ years}$$

Substitution of values

$$\lambda = \frac{0.693}{5760 \text{ years}} = 1.203 \times 10^{-4} \text{ year}^{-1}$$

(ii) To calculate the age of the wooden article

Formula used

$$\lambda = \frac{2.303}{t} \log \frac{N^0}{N}$$

or

$$t = \frac{2.303}{\lambda} \log \frac{N^0}{N}$$

Quantities given

$$\lambda = 1.203 \times 10^{-4} \text{ year}^{-1}$$

$$N^0 = 15.2 \text{ Counts per min per g}$$

$$N = 2.0 \text{ Counts per min per g}$$

Substitution of values

$$\begin{aligned} t &= \frac{2.303}{1.203 \times 10^{-4} \text{ year}^{-1}} \log \frac{15.2}{2} \\ &= \frac{2.303}{1.203 \times 10^{-4} \text{ year}^{-1}} \log 7.6 \\ &= \frac{2.303}{1.203 \times 10^{-4} \text{ year}^{-1}} \times 0.8808 \\ &= 1.943 \times 10^4 \text{ year} \times 0.8808 \\ &= \mathbf{16862 \text{ years}} \end{aligned}$$

SOLVED PROBLEM 24. ${}_{92}\text{U}^{238}$ by successive radioactive decay changes to ${}_{82}\text{Pb}^{206}$. A sample of uranium ore was analyzed and found to contain 1 g of U^{238} and 0.1 g of Pb^{206} . Assuming that all Pb^{206} had accumulated due to decay of U^{238} find out age of the ore. (Half life of $\text{U}^{238} = 4.5 \times 10^9$ years).

SOLUTION :

(i) To calculate the disintegration constant

Formula used

$$\lambda = \frac{0.693}{t_{1/2}}$$

Quantity given

$$t_{1/2} = 4.5 \times 10^9 \text{ years}$$

Substitution of values

$$\begin{aligned} \lambda &= \frac{0.693}{4.5 \times 10^9 \text{ years}} \\ &= \mathbf{0.154 \times 10^{-9} \text{ year}^{-1}} \end{aligned}$$

(ii) To calculate the initial amount of U^{238} , N^0

Since the whole of Pb^{206} comes from U^{238}

$$\begin{aligned}
 \text{Amount of } \text{U}^{238} \text{ decayed} &= \text{Amount of } \text{Pb}^{206} \text{ formed} \\
 \therefore \text{Amount of } \text{U}^{238} \text{ decayed} &= \frac{0.1 \times 238}{206} \text{ g} \\
 &= 0.1155 \text{ g} \\
 \text{and the initial amount of } \text{U}^{238} &= 1 \text{ g} + 0.1155 \text{ g} \\
 N^0 &= 1.1155 \text{ g}
 \end{aligned}$$

(iii) To calculate the age of the ore

Formula used

$$\lambda = \frac{2.303}{t} \log \frac{N^0}{N}$$

or

$$t = \frac{2.303}{\lambda} \log \frac{N^0}{N}$$

Quantities given

$$\lambda = 0.154 \times 10^{-9} \text{ year}^{-1}$$

$$N^0 = 1.1155 \text{ g}$$

$$N = 1 \text{ g}$$

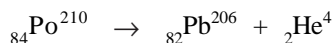
Substitution of values

$$\begin{aligned}
 t &= \frac{2.303}{0.154 \times 10^{-9} \text{ year}^{-1}} \log \frac{1.1155}{1} \\
 &= 14.95 \times 10^9 \text{ year} \times 0.0474 \\
 &= \mathbf{7.09 \times 10^8 \text{ years}}
 \end{aligned}$$

SOLVED PROBLEM 25. Po^{210} decays with alpha to $_{82}\text{Pb}^{206}$ with a half life of 138.4 days. If 1.0 g of Po^{210} is placed in a sealed tube, how much helium will accumulate in 69.2 days ? Express the answer in cm^3 at STP.

SOLUTION :

The nuclear equation is



(i) To calculate the decay constant

Formula used

$$\lambda = \frac{0.693}{t_{1/2}}$$

Quantity given

$$t_{1/2} = 138.4 \text{ days}$$

Substitution of values

$$\begin{aligned}
 \lambda &= \frac{0.693}{138.4 \text{ days}} \\
 &= 5.0 \times 10^{-3} \text{ day}^{-1}
 \end{aligned}$$

(ii) To calculate the amount of $_{84}\text{Po}^{210}$ left after 69.2 days

Formula used

$$\lambda = \frac{2.303}{t} \log \frac{N^0}{N}$$

Quantities given

$$\lambda = 5.0 \times 10^{-3} \text{ day}^{-1}$$

$$t = 69.2 \text{ days}$$

Substitution of values

$$5.0 \times 10^{-3} \text{ day}^{-1} = \frac{2.303}{69.2 \text{ days}} \log \frac{N^0}{N}$$

$$\text{or} \quad \log \frac{N^0}{N} = \frac{5.0 \times 10^{-3} \text{ day}^{-1} \times 69.2 \text{ day}}{2.303}$$

$$\log \frac{N^0}{N} = 1.502 \times 10^{-1} = 0.1502$$

$$\text{or} \quad \frac{N^0}{N} = \text{Antilog } 0.1502$$

$$= 1.413$$

$$\text{or} \quad \frac{N}{N^0} = \frac{1}{1.413} = 0.707$$

$$\text{or} \quad N = N^0 \times 0.707$$

$$= 1 \text{ g} \times 0.707 \quad [\because N^0 = 1 \text{ g given}]$$

$$= 0.707 \text{ g}$$

$$\text{Mass of } {}_{84}\text{Po}^{210} \text{ decomposed to } {}_2\text{He}^4$$

$$= 1 \text{ g} - 0.707 \text{ g}$$

$$= 0.293 \text{ g}$$

(iii) To calculate the volume of ${}_2\text{He}^4$ accumulated at STP

$$\text{i.e.} \quad 210 \text{ g of } {}_{84}\text{Po}^{210} = {}_2\text{He}^4$$

$$= 4 \text{ g of } {}_2\text{He}^4$$

$$\therefore 0.293 \text{ g of } {}_{84}\text{Po}^{210} = \frac{4}{210} \times 0.293 \text{ g of } {}_2\text{He}^4$$

$$= 5.580 \times 10^{-3} \text{ g}$$

$$\text{At STP} \quad 4 \text{ g of } {}_2\text{He}^4 = 22400 \text{ cm}^3$$

$$\therefore 5.580 \times 10^{-3} \text{ g of } {}_2\text{He}^4 = \frac{22400}{4} \times 5.580 \times 10^{-3} \text{ cm}^3$$

$$= 31.248 \text{ cm}^3$$

SOLVED PROBLEM 26. In nature a decay chain series start with ${}_{90}\text{Th}^{232}$ and finally terminates at ${}_{82}\text{Pb}^{208}$. A thorium ore sample was found to contain $8 \times 10^5 \text{ ml}$ of helium at STP and of Th^{232} . Find the age of the sample assuming the source of helium to be only due to the decay of Th^{232} . Also assume complete retention of helium within the ore. (Half life of $\text{Th}^{232} = 1.39 \times 10^{10} \text{ ml}$).

SOLUTION :

(i) To calculate the decay constant

$$\text{Formula used} \quad \lambda = \frac{0.693}{t_{1/2}}$$

Quantity given

$$t_{1/2} = 1.39 \times 10^{10} \text{ year}$$

Substitution of values

$$\lambda = \frac{0.693}{1.39 \times 10^{10} \text{ year}}$$

$$= 4.986 \times 10^{-11} \text{ year}^{-1}$$

(ii) To calculate the no. of Th^{232} used up and left

$$\text{No. of helium atoms in } 8 \times 10^5 \text{ ml at STP} = \frac{8 \times 10^5 \times 6.02 \times 10^{23}}{22400}$$

$$[\because 22400 \text{ ml} = 6.02 \times 10^{23} \text{ atoms}]$$

$$= 2.15 \times 10^{15} \text{ atoms}$$

$$\begin{aligned}
 \text{No. of Th}^{232} \text{ atoms used up} &= \frac{2.15 \times 10^{15} \text{ atoms}}{6} \\
 &= 3.583 \times 10^{14} \text{ atoms} \\
 \text{No. of Th}^{232} \text{ atoms left (N)} &= \frac{5 \times 10^{-7} \times 6.02 \times 10^{23}}{232} \\
 &\quad [5 \times 232 \text{ g of Th} = 6.02 \times 10^{23} \text{ atoms}] \\
 &= 1.297 \times 10^{15} \text{ atoms} \\
 \text{No. of Th}^{232} \text{ atoms at the beginning (N}^0\text{)} &= 3.583 \times 10^{14} + 1.297 \times 10^{15} \text{ atoms} \\
 &= 16.553 \times 10^{14} \text{ atoms}
 \end{aligned}$$

(iii) To calculate the age of the sample

Formula used

$$\begin{aligned}
 \lambda &= \frac{2.303}{t} \log \frac{N^0}{N} \\
 \text{or} \quad t &= \frac{2.303}{\lambda} \log \frac{N^0}{N}
 \end{aligned}$$

Quantities given

$$\lambda = 4.985 \times 10^{-11} \text{ year}^{-1} \quad N^0 = 16.553 \times 10^{14} \text{ atoms} \quad N = 1.297 \times 10^{15} \text{ atoms}$$

Substitution of values

$$\begin{aligned}
 t &= \frac{2.303}{4.985 \times 10^{-11} \text{ year}^{-1}} \times \log \frac{16.553 \times 10^{14} \text{ atom}}{1.297 \times 10^{14} \text{ atom}} \\
 &= 4.6199 \times 10^{10} \text{ year} \times 0.1059 \\
 &= \mathbf{4.892 \times 10^9 \text{ years}}
 \end{aligned}$$

SOLVED PROBLEM 27. A sample of U^{238} (half life = 4.5×10^9 years) ore is found to contain 23.8 g of U^{238} and 20.6 g of Pb^{206} . Calculate the age of the ore.

SOLUTION :

Formula used

$$\lambda = \frac{0.693}{t_{1/2}}$$

Quantity given

$$t_{1/2} = 4.5 \times 10^9 \text{ years}$$

Substitution of values

$$\begin{aligned}
 \lambda &= \frac{0.693}{4.5 \times 10^9 \text{ years}} \\
 &= 0.154 \times 10^{-9} \text{ year}^{-1} \\
 &= 1.54 \times 10^{-10} \text{ year}^{-1}
 \end{aligned}$$

(ii) To calculate the number of moles of U^{238} disintegrated and left

Since



$$\begin{aligned}
 \text{and } 20.6 \text{ g of Pb}^{206} &= \frac{20.6 \text{ g}}{206 \text{ g mol}^{-1}} = 0.1 \text{ mole} \\
 \therefore \text{ no. of mole of U}^{238} \text{ disintegrated} &= 0.1 \text{ mole} \\
 \text{and the initial no. of moles of U}^{238} &= \text{no. of moles of U}^{238} \text{ left} + \\
 &\quad \text{no. of moles of U}^{238} \text{ integrated} \\
 &= 0.1 + 0.1 \text{ mol} \\
 &= 0.2 \text{ mol}
 \end{aligned}$$

(iii) To calculate the age of the ore**Formula used**

$$\lambda = \frac{2.303}{t} \log \frac{N^0}{N}$$

or

$$t = \frac{2.303}{\lambda} \log \frac{N^0}{N}$$

Quantities given

$$\lambda = 1.54 \times 10^{-10} \text{ year}^{-1}$$

$$N^0 = 0.2 \text{ mol}$$

$$N = 0.1 \text{ mol}$$

Substitution of values

$$\begin{aligned} t &= \frac{2.303}{1.54 \times 10^{-10} \text{ year}^{-1}} \log \frac{0.2 \text{ mol}}{0.1 \text{ mol}} \\ &= 1.4955 \times 10^{10} \text{ year} \times \log 2 \\ &= 1.4955 \times 10^{10} \times 0.3010 \text{ years} \\ &= 0.450 \times 10^{10} \text{ years} \\ &= \mathbf{4.50 \times 10^9 \text{ years}} \end{aligned}$$

SOLVED PROBLEM 28. An experiment requires minimum Beta activity produced at the rate of 346 Beta particles per minute. The half life of $_{42}\text{Mo}^{99}$, which is a Beta emitter is 66.6 hours. Find the minimum amount of $_{42}\text{Mo}^{99}$ required to carry out the experiment 6.909 hours.

SOLUTION :**(i) To calculate the disintegration constant****Formula used**

$$\lambda = \frac{0.693}{t_{1/2}}$$

Quantity given

$$t_{1/2} = 66.6 \text{ hours} = 66.6 \times 60 \text{ min} = 3996 \text{ min}$$

Substitution of values

$$\begin{aligned} \lambda &= \frac{0.693}{3996 \text{ min}} \\ &= 1.734 \times 10^{-4} \text{ min}^{-1} \end{aligned}$$

(ii) To calculate the activity required

Time required for the completion of experiment

$$\begin{aligned} &= 6.909 \text{ hours} \\ &= 6.909 \times 60 \text{ min} \\ &= 414.54 \text{ min} \end{aligned}$$

$$\text{Total activity required} = 346 \times 414.54 \text{ Beta particles}$$

$$= 1.4343 \times 10^5 \text{ Beta particles}$$

(iii) To calculate the amount of $_{42}\text{Mo}^{99}$ required**Formula used**

$$\begin{aligned} \text{Activity} &= \lambda \times N \\ \text{or} \quad N &= \frac{\text{Activity}}{\lambda} \end{aligned}$$

Quantities given

$$\text{Activity} = 1.4343 \times 10^5 \beta \text{ particles} \quad \lambda = 1.734 \times 10^{-4} \text{ min}^{-1}$$

Substitution of values

$$N = \frac{1.4343 \times 10^5 \beta \text{ particles}}{1.734 \times 10^{-4} \text{ min}^{-1}}$$

$$\begin{aligned}
 \therefore \text{No. of moles of } {}_{42}\text{Mo}^{99} \text{ required} &= 8.27 \times 10^8 \beta \text{ particles} \\
 &= \frac{8.27 \times 10^8}{6.02 \times 10^{23} \text{ mol}^{-1}} \\
 &= 1.37 \times 10^{-15} \text{ mol}
 \end{aligned}$$

$$\begin{aligned}
 \text{and Amount of } {}_{42}\text{Mo}^{99} \text{ required} &= 1.37 \times 10^{-15} \text{ mol} \times 99 \text{ g mol}^{-1} \\
 &= \mathbf{135.63 \times 10^{-15} \text{ g}}
 \end{aligned}$$

SOLVED PROBLEM 29. The nucleidic ratio ${}_1\text{H}^3$ to ${}_1\text{H}^1$ in a sample of water is . Tritium undergoes decay with half life period of 12.3 years. How many tritium atoms would 10 g of such a sample contain 40 years after the original sample is collected.

SOLUTION :

(i) To calculate the disintegration constant

Formula used

$$\lambda = \frac{0.693}{t_{1/2}}$$

Quantity given

$$t_{1/2} = 12.3 \text{ years}$$

Substitution of values

$$\begin{aligned}
 \lambda &= \frac{0.693}{12.3 \text{ years}} \\
 &= 5.634 \times 10^{-2} \text{ year}^{-1}
 \end{aligned}$$

(ii) To calculate the number of Tritium atoms

$$\text{No. of moles of water in 10 g sample} = \frac{10}{18} \text{ mole}$$

$$\text{No. of moles of H atoms in 10 g sample} = \frac{2 \times 10}{18} \text{ mole}$$

$$\text{As } {}_1\text{H}^3 : {}_1\text{H}^1 = 8 \times 10^{-18} : 1$$

$$\begin{aligned}
 \therefore \text{the no. of tritium atoms} &= \frac{8 \times 10^{-18} \times 2 \times 10 \times 6.02 \times 10^{23}}{18} \\
 &= 5.35 \times 10^6 \text{ atoms}
 \end{aligned}$$

(iii) To calculate the number of Tritium atoms left after 40 years

Formula used

$$\lambda = \frac{2.303}{t} \log \frac{N^0}{N}$$

Quantities given

$$\lambda = 5.634 \times 10^{-2} \text{ year}^{-1} \quad t = 40 \text{ years} \quad N^0 = 5.35 \times 10^6 \text{ atoms}$$

Substitution of values

$$5.634 \times 10^{-2} \text{ year}^{-1} = \frac{2.303}{40 \text{ years}} \log \frac{N^0}{N}$$

$$\begin{aligned}
 \text{or } \log \frac{N^0}{N} &= \frac{5.634 \times 10^{-2} \text{ year}^{-1} \times 40 \text{ years}}{2.303} \\
 &= 0.9785
 \end{aligned}$$

$$\text{or } \log \frac{N}{N^0} = 0.9785$$

$$\begin{aligned}
 \text{or} \quad \frac{N}{N^0} &= \text{Antilog}(-0.9785) \\
 &= 0.1050 \\
 \text{or} \quad N &= N^0 \times 0.1050 \\
 &= 5.35 \times 10^6 \times 0.1050 \\
 &= \mathbf{5.6175 \times 10^5 \text{ atoms}}
 \end{aligned}$$

SOLVED PROBLEM 30. One of the hazards of nuclear explosion is the generation of Sr^{90} and its subsequent incorporation in bones. This nuclide has half life of 28.1 years. Suppose one microgram was absorbed by a new born child, how much Sr^{90} will remain in his bones after 20 years.

SOLUTION :

(i) To calculate the disintegration constant

Formula used

$$\lambda = \frac{0.693}{t_{1/2}}$$

Quantity given

$$t_{1/2} = 28.1 \text{ years}$$

Substitution of values

$$\begin{aligned}
 \lambda &= \frac{0.693}{28.1 \text{ years}} \\
 &= 0.0246 \text{ year}^{-1}
 \end{aligned}$$

(ii) To calculate the amount of Sr^{90} left after 20 years

Formula used

$$\lambda = \frac{2.303}{t} \log \frac{N^0}{N}$$

Quantities given

$$\lambda = 0.0246 \text{ year}^{-1}$$

$$N^0 = 1 \text{ g}$$

$$t = 20 \text{ years}$$

Substitution of values

$$0.0246 \text{ year}^{-1} = \frac{2.303}{20 \text{ years}} \times \log \frac{N^0}{N}$$

$$\begin{aligned}
 \text{or} \quad \log \frac{N^0}{N} &= \frac{0.0246 \text{ year}^{-1} \times 20 \text{ years}}{2.303} \\
 &= 0.2136
 \end{aligned}$$

$$\text{or} \quad \frac{N^0}{N} = \text{Antilog } 0.2136$$

$$\text{or} \quad \frac{N^0}{N} = 1.635$$

$$\text{or} \quad \frac{N}{N^0} = \frac{1}{1.635} = 0.61$$

$$\begin{aligned}
 \text{or} \quad N &= N^0 \times 0.61 \\
 &= 1 \mu\text{g} \times 0.61 \\
 &= \mathbf{0.61 \mu\text{g}}
 \end{aligned}$$

SOLVED PROBLEM 31. Ac^{227} has a half life of 21.8 years with respect to radioactive decay. The decay follows two parallel paths, one leading to Th^{227} and the other leading to Fr^{223} . The percentage yield of these two daughter nucleides are 1.2% and 98.8% respectively. What is the rate constant, in year^{-1} , for each of the separate path.

SOLUTION :**(i) To calculate the rate constant for Ac^{227} decay****Formula used**

$$k = \lambda = \frac{0.693}{t_{1/2}}$$

Quantity given

$$t_{1/2} = 21.8 \text{ years}$$

Substitution of values

$$\begin{aligned} k &= \frac{0.693}{21.8 \text{ years}} \\ &= 3.178 \times 10^{-2} \text{ year}^{-1} \end{aligned}$$

(ii) To calculate the rate constants for Th^{227} and Fr^{223} .

For a first order parallel reaction, the overall rate constant is equal to the sum of rate constant for separate paths *i.e.*

$$\begin{aligned} K_{Ac} &= k_{Th} + k_{Fr} \\ k_{Th} &= \% \text{age yield} \times K_{Ac} \\ &= \frac{1.2}{100} \times 3.178 \times 10^{-2} \text{ year}^{-1} \\ &= \mathbf{3.814 \times 10^{-2} \text{ year}^{-1}} \end{aligned}$$

and

$$\begin{aligned} k_{Fr} &= \% \text{age yield} \times K_{Ac} \\ &= \frac{98.8}{100} \times 3.178 \times 10^{-2} \text{ year}^{-1} \\ &= \mathbf{3.139 \times 10^{-2} \text{ year}^{-1}} \end{aligned}$$

ADDITIONAL PRACTICE PROBLEMS

- Calculate the number of α and β particles emitted in the conversion of Thorium, ${}_{90}\text{Th}^{232}$, to lead, ${}_{82}\text{Pb}^{206}$.
Answer: 6 α , 4 β
- The mass number and atomic number of a radioactive element Actinium are 227 and 89 respectively. Calculate the number of α and β particles emitted if the mass number and atomic number of the new element lead are 207 and 82 respectively.
Answer: 5 α , 3 β
- ${}_{92}\text{U}^{238}$ undergoes a series of change emitting α and β particles and finally ${}_{82}\text{Pb}^{206}$ is formed. Calculate the number of α and β particles which must have been ejected during the series.
Answer: 8 α , 6 β
- The half life of cobalt-60 is 5.26 years. Calculate the percentage activity after eight years.
Answer: 34.87%

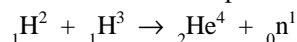
5. An old wooden article shows 2.0 counts per minute per gram. A fresh sample of wood shows 15.2 counts per minute per gram. Calculate the age of the wooden article. (of $C^{14} = 5760$ years)

Answer. 1686.6 years

6. Calculate the age of the tooth in which C^{14} activity is 20% of the activity found at the present time (for $C^{14} = 5580$ years)

Answer. 12961.4 years

7. Calculate the energy released in the fusion reaction per atom of helium produced.



Given the following atomic masses

${}_1H^2 = 2.014$; ${}_1H^3 = 3.016$; ${}_2He^4 = 4.003$; ${}_0n^1 = 1.009$ amu and
 $1 \text{ amu} = 1.51 \times 10^{-10} \text{ J}$.

Answer. $2.72 \times 10^{-12} \text{ J}$

8. Calculate the rate of disintegration of one gram of Th^{232} if its decay constant is $1.58 \times 10^{-18} \text{ sec}^{-1}$.

Answer. $4.0998 \times 10^3 \text{ dps}$

9. The activity of a radioactive sample falls to 85% of the initial value in four years. What is the half life of the sample? Calculate the time by which activity will fall to 85%.

Answer. 17.05 years; 46.735 years

10. 2 g of a radioactive element degraded to 0.5 g in 60 hours. In what time will it be reduced to 10% of its original amount?

Answer. 4.56 hours

11. Calculate the time required for a radioactive sample to lose one-third of the atoms of its parent isotope. The half life is 33 min.

Answer. 19.31 min

12. A piece of wood recovered in excavation has 30% as much ${}_6C^{14}$ as a fresh wood today. Calculate the age of excavated piece assuming half life period of ${}_6C^{14}$ as 5700 years.

Answer. 9908 years

13. Radioisotope ${}_{15}P^{32}$ has a half life of 15 days. Calculate the time in which the radioactivity of its 1 mg quantity will fall to 10% of the initial value.

Answer. 49.84 days

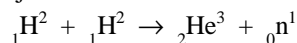
14. A natural isotope of potassium has a half life of years. Out of 1 mole of this isotope, how many atoms will remain after 10^{11} years?

Answer. 1.258×10^{23} atoms

15. In the fission of ${}_{92}U^{235}$ with thermal neutron, the products are Mo^{95} , La^{139} and two neutrons. Calculate the energy released in MeV in the fission of 1 g ${}_{92}U^{235}$. The atomic masses in amu are $U = 235$; $Mo = 94.936$; $La = 138.950$; ${}_0n^1 = 1.009$.

Answer. $5.32 \times 10^{23} \text{ MeV}$

16. Calculate the energy released in joules and MeV in the following nuclear reaction:



Assume that masses of ${}_1H^2$, ${}_2He^3$, and ${}_0n^1$ are 2.0141, 3.0160 and 1.0087 in amu.

Answer. $5.22 \times 10^{-3} \text{ J}$; 3.2585 MeV

5

Chemical Bonding

CHAPTER

KEY CONCEPTS AND EQUATIONS



CHEMICAL BOND AND VALENCE

The force which results from the interaction between various atoms that form a stable molecule is referred to as a chemical bond. It is defined as a force that holds two or more atoms together as a stable molecule.

The valence is the number of bonds formed by an atom in a molecule.

OCTET RULE

Atoms interact by electron transfer or sharing so as to have the stable outer shell of eight electrons. This tendency for atoms to have eight electrons in the outer shell is known as **Octet rule**.

IONIC BOND

The electrostatic attraction between the cations and anions produced by electron transfer constitutes an **Ionic** or **Electrostatic bond**. Following factors favour the formation of Ionic bond.

(i) The ionisation energy of the metal atom which loses electrons should be low. That is why alkali metals and alkaline earth metals form Ionic bonds. The tendency to form ionic bond increases as we go down a group as there is a decrease in Ionisation energy.

(ii) The electron affinity of the electron accepting atom should be high. The elements of group VI A and VII B have high electron affinity. That is why they form ionic bonds with the metals. In moving down a group the electron affinity decreases and, therefore, the tendency to form ionic bond decrease.

(iii) The Lattice Energy is the amount of energy released when one mole of an ionic compound is formed from its cations and anions. Greater the lattice energy, greater the strength of the ionic bond.

COVALENT BOND

The covalent bond is attractive force between atom created by sharing of an electron pair. It is indicated by a dash (–) between the two bonded atoms. After sharing both atoms have eight electrons in their outer most shell.

CONDITIONS FOR THE FORMATION OF COVALENT BOND

(i) Each of the atoms should have 5, 6 or 7 valence electrons so as to have eight electrons by sharing 3, 2 or 1 electron pair. The non-metals of group VA, VIA and VIIA satisfy this condition and form covalent bonds.

- (ii) Both the atom should have same for similar electronegativity.
- (iii) Both the atoms should have equal or almost equal electron affinity.

EXAMPLES OF COVALENT COMPOUNDS

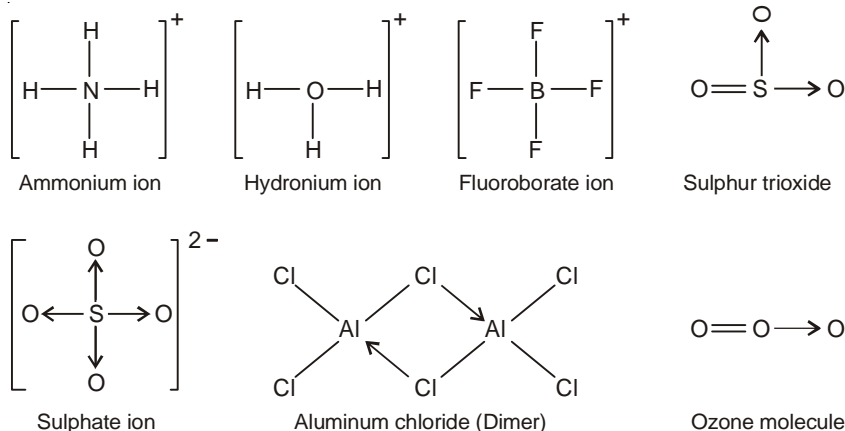


COORDINATE COVALENT BOND

In some cases a covalent bond is formed when both the electrons are supplied by one atom and sharing is done by both the atoms. Such a bond is called **Coordinate covalent bond** or **dative bond**. The atom which donates a pair of electrons is called **donor**, while the atoms which accepts the electron pair is called **acceptor**. This type of bond is represented by an arrow pointing towards the acceptor atom.



EXAMPLES OF COORDINATE COVALENT COMPOUNDS OR IONS



POLAR COVALENT BOND

A covalent bond in which electrons are shared unequally and the bonded atoms acquire a partial positive and negative charge is called a polar covalent bond. The polarity of a bond is determined by the difference in electronegativity of the two bonded atoms.

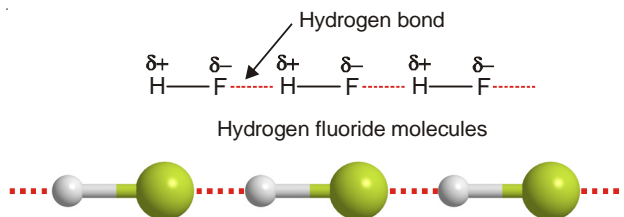
The percentage Ionic character of a bond can be calculated by using the equation

$$\% \text{age Ionic character} = 16 [X_A - X_B] + 3.5 [X_A + X_B]^2$$

where X_A and X_B are the electronegativities of the two atoms.

HYDROGEN BONDING

The electrostatic attraction between a H atom covalently bonded to a highly electronegative atom X and lone pair of electrons on X in another molecule is called **Hydrogen bonding**. It is represented by a dotted line.



CONDITIONS OF HYDROGEN BONDING

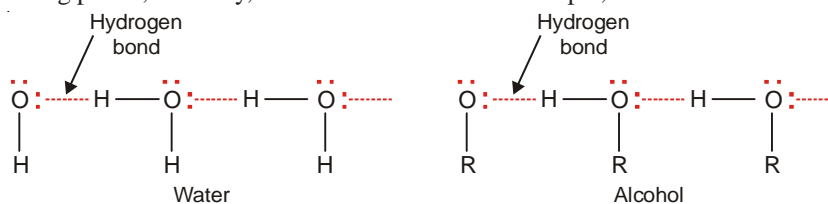
(1) The electronegativity of the atom bonded to H atom should be high. The atoms such as F, O and N form Hydrogen Bonding.

(2) The size of the atom bonded by H atom should be small. For example, N and Cl both have 3.0 electronegativity but H-bonding is effective in NH_3 due to smaller size of N atoms than Cl atom.

TYPES OF HYDROGEN BONDING

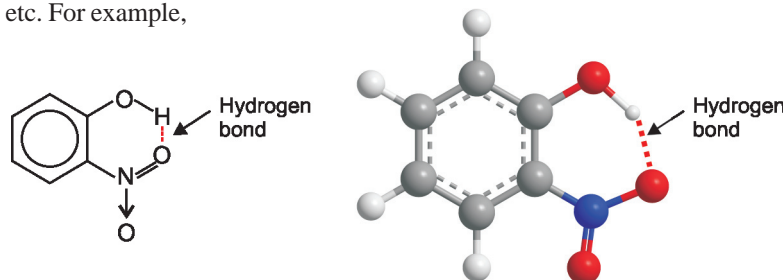
(1) Intermolecular H-bonding

This type of bonding occurs in two different molecules of the same or different substances. It results in the associated molecules. The substances having inter molecular H-bonding have high melting or boiling points, viscosity, surface tension etc. For example,



(2) Intramolecular H-bonding

This type of hydrogen bonding is formed between the H atoms and electronegative atom present within the same molecule. It results in cyclization of the molecule. Molecules exist as discrete unit and not in associated form. Intramolecular H-bonding has no effect of melting and boiling points, viscosity, surface tension, etc. For example,



GEOMETRY OF MOLECULES VSEPR THEORY

It states that the electron pairs both lone pairs and bond pairs surrounding the central atom will be arranged in space as far apart as possible to minimise the electrostatic repulsion between them. On the basis of VSEPR theory the shapes of some molecules with their bond angles are given in Table 5.1

TABLE 5.1 SHAPES OF MOLECULES - VSEPR THEORY

Molecule	No. of electron pairs around central atom	Shape of the molecule	Bond Angle
BeCl_2	2	Linear	180°
BF_3, SO_3	3	Trigonal Planar	120°
CH_4	4	Tetrahedral	$109^\circ 28'$
NH_3	4	Distorted Tetrahedral	107°
H_2O	4	Distorted Tetrahedral	105°
PF_5	5	Trigonal Bipyramidal	$90^\circ, 120^\circ$
SF_6	6	Octahedral	90°

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. Two elements X and Y occur in same period and their atoms have two and seven valence electrons respectively. Write down the most probable compound between X and Y. Will the bond between X and Y be predominantly ionic or covalent ?

SOLUTION :

Since the element X has two electrons in the valence shell, it should be electropositive and have a tendency to form X^{2+} by losing two electrons.

The element Y has seven electrons in the valence shell, it should be electronegative and have a tendency to form Y^- by gaining one electron.

X^{2+} combines with two Y^- anions to form the compound with formula XY_2 .

Since the bond has been formed by the transfer of electrons the bond is purely **ionic**.

SOLVED PROBLEM 2. Calculate the percentage ionic character of C—Cl bond in CCl_4 , if the electronegativities of C and Cl are 3.5 and 3.0 respectively.

SOLUTION :**Formula used**

$$\% \text{ age ionic character} = 16 [X_A - X_B] + 3.5 [X_A - X_B]^2$$

Quantities given

$$X_A = 3.5 \quad X_B = 3.0$$

Substitution of values

$$\begin{aligned} \% \text{ age Ionic Character} &= 16(3.5 - 3.0) + 3.5 (3.5 - 3.0)^2 \\ &= 8.0 + 0.875 \\ &= \mathbf{8.875\%} \end{aligned}$$

SOLVED PROBLEM 3. The dipole moment of KCl is 3.336×10^{-29} coulomb meter which indicates that it is highly polar molecule. The interionic distance between K^+ and Cl^- in this molecule is 2.6×10^{-10} m. Calculate the dipole moment of KCl molecule if there were opposite charges of one fundamental unit localised at each nucleus. Calculate the percentage ionic character of KCl.

SOLUTION :**Formula used :**

$$\mu = e \times d$$

For complete separation of unit charge (100% ionic character)

$$\begin{aligned} \mu &= 1.602 \times 10^{-19} \text{ coulomb} \times 2.6 \times 10^{-10} \text{ m} \\ &= 4.165 \times 10^{-29} \text{ coulomb meter} \end{aligned}$$

Quantity given

$$\text{Actual dipole moment of KCl} = 3.336 \times 10^{-29} \text{ coulomb meter.}$$

Substitution of values

$$\begin{aligned} \% \text{ ionic character of KCl} &= 100 \times \frac{3.336 \times 10^{-29} \text{ coulomb meter}}{4.165 \times 10^{-29} \text{ coulomb meter}} \\ &= \mathbf{80\%} \end{aligned}$$

SOLVED PROBLEM 4. Write the two resonance structures of N_2O that satisfy the octet rule.

SOLUTION :

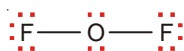
The two resonating structures are



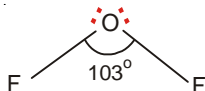
SOLVED PROBLEM 5. Using VSEPR theory, identify the type of hybridisation and draw the structure of OF_2 . What are the oxidation states of O and F ?

SOLUTION :

The dot Lewis diagram of OF_2 is



There are two lone pairs and two bond pairs around central oxygen atom. Thus the hybridisation will be sp^3 and the shape will be distorted tetrahedral due to the presence of lone pairs of electrons. The angle FOF is 103° and it is V-shaped molecule.



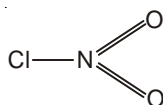
SOLVED PROBLEM 6. Account for : The experimentally found N — F bond length in NF_3 is greater than the sum of single covalent radii of N and F.

SOLUTION :

The bond length of N — F bond in NF_3 molecule is greater than the sum of single covalent radii of N and F is due to repulsion of the bond pair by both Nitrogen and Fluorine atom. It is due to smaller size and high electron density around N atom.

ADDITIONAL PRACTICE PROBLEMS

- Write the Lewis structure for carbon tetrachloride, CCl_4 and formaldehyde, HCHO .
- Which of the following compounds contain bonds that are predominantly ionic in character : MgO , Ca_3P_2 , AlCl_3 , Mg_2Si and CsF .
Answer. CsF , Mg_2Si and MgO
- Classify the bonds in the following as ionic, polar covalent or covalent : (a) HCl (b) NaCl and (c) NCl_3 .
Answer. HCl - Polar covalent, NaCl - Ionic and NCl_3 - Covalent
- Draw the Lewis structure for NO_3^- and PO_4^{3-} ions.
- Complete the following structural formula by adding unshared electron pairs to the structures given.



6. The experimentally determined dipole moment, μ , of KF is 2.87×10^{-29} coulomb meter. The distance, d , separating the centers of charge in a KF dipole is 2.66×10^{-3} m. Calculate the percent ionic character of KF.

Answer. 67.4%

7. Write the Lewis formula for Thionyl chloride, SOCl_2 , and Carbonyl chloride COCl_2 .

8. Predict the geometry of the following molecules using VSEPR theory.

(a) CCl_4 (b) AlCl_3 (c) H_2Se .

Answer. (a) Tetrahedral (b) Trigonal planar (c) Bent

9. What geometry is expected for the following molecules according to the VSEPR theory ?

(a) PF_5 (b) SCl_4 (c) BrF_3

Answer. (a) Trigonal bipyramidal (b) See-saw (c) T-Shaped

10. Predict the geometry of the following ions having VSEPR model.

(a) H_3O^+ (b) NO_2^- (c) ClO_2^-

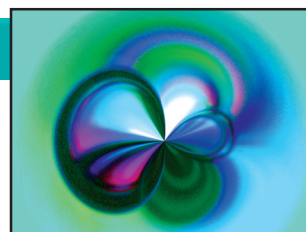
Answer. (a) Pyramidal (b) Bent (c) Bent

6

Chemical Bonding – Orbital Concept

CHAPTER

KEY CONCEPTS AND EQUATIONS



CHEMICAL BONDING – ENERGY CONCEPT

Two or more atoms unite to form a molecule because in doing so the energy of the system decreases and the molecule becomes stable as compared to isolated atoms. The amount of energy released per mole is termed as Bond energy or stabilisation energy.

ATOMIC ORBITAL THEORY

According to this theory a bond is formed when atomic orbital of one atom overlaps with the atomic orbital of the other atom. The strength of the bond depends upon the extent of overlapping. Greater the extent of overlap, greater the strength of the bond.

TYPES OF OVERLAPPING AND NATURE OF COVALENT BOND

A covalent bond is of two types depending on the type of overlapping between two atoms.

1. Sigma (σ) bond

This type of covalent bond results when there is end to end overlapping of atomic orbitals along the internuclear axis. It is formed when s - s , s - p or p - p head-on overlapping takes place.

2. Pi (π) bond

This type of covalent bond results when there is sidewise overlap of half filled atomic orbitals. It is formed when p - p sidewise overlapping takes place. This bond is weaker than sigma bond.

HYBRIDISATION AND SHAPE OF MOLECULES

It may be defined as the concept of mixing up of orbitals of nearly equal energy giving rise to new orbitals which are having equal energy and identical shapes. Depending upon the number and nature of the orbitals undergoing hybridisation we have various types of hybrid orbitals. The details are summarised in Table 6.1

TABLE 6.1. HYBRIDISATION AND SHAPE OF MOLECULES

Type of Hybridisation	No. and type of Orbitals mixed	No. and type of New orbitals formed	Shape	Examples
sp	s and p	sp Two	Linear	$\text{BeF}_2, \text{BeCl}_2, \text{C}_2\text{H}_2$
sp^2	s and two p	sp^2 Three	Trigonal	BF_3
sp^3	s and three p	sp^3 Four	Tetrahedral	$\text{CH}_4, \text{SO}_4^{2-}, \text{ClO}_4^{2-}$
sp^3d	s , three p and one d	sp^3d Five	Trigonal bipyramidal	PF_5
sp^3d^2	s , three p and two d	sp^3d^2 Six	Octahedral	SF_6

MOLECULAR ORBITAL THEORY

According to this theory all atomic orbitals of the participating atoms mix up and give rise to an equivalent number of new orbitals belonging to the molecule. These new orbitals are called molecular orbitals. These are of two types.

(i) **Bonding Molecular orbital** formed by the addition of wave functions of atomic orbitals. It lowers the energy and is responsible for the stability in the system.

(ii) **Anti-Bonding Molecular orbital** formed by the subtraction of wave function of atomic orbitals. It has net disruptive effect.

Since we are concerned with the few simple molecules, the only molecular orbitals which need to be considered are

$$\text{Bonding MOs} = \sigma(1s) \sigma(2s) \sigma(2p_z) \pi 2p_y \pi 2p_x$$

$$\text{Antibonding MOs} = \sigma^*(1s) \sigma^*(2s) \sigma^*(2p_z) \pi^* 2p_y \pi^* 2p_x$$

These are arranged in their increasing order of energy as determined by spectroscopic measurements.

$$\sigma(1s) \sigma^*(1s) \sigma(2s) \sigma^*(2s) \sigma(2p_z) \pi(2p_y) = \pi(2p_x) \pi^*(2p_y) = \pi^*(2p_x) \sigma^*(2p_z)$$

BOND ORDER

The term bond order refers to the number of bonds that exist between two atoms. In molecular orbital theory the bond order is one half of the difference of the number of electrons in the bonding molecular orbitals and the number of electrons in the antibonding molecular orbitals. Mathematically,

$$\text{Bond Order} = \frac{N_b - N_a}{2}$$

where N_b is the number of electrons in bonding MOs

and N_a is the number of electrons in antibonding MOs.

The electronic configuration and bond order of various molecules have been summarized in Table 6.2

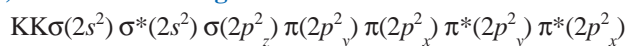
TABLE 6.2. ELECTRONIC CONFIGURATION AND BOND ORDERS

Molecule / Ion	Electronic Configuration	Bond Order
H ₂	$\sigma(1s^2) \sigma^*(1s^0)$	$\frac{2-0}{2} = 1$
He ₂	$\sigma(1s^2) \sigma^*(1s^2)$	$\frac{2-2}{2} = 0$
Li ²	$KK\sigma(2s^2) \sigma^*(2s^0)$	$\frac{2-0}{2} = 1$
Be ₂	$KK\sigma(2s^2) \sigma^*(2s^2)$	$\frac{2-2}{2} = 0$
N ₂	$KK\sigma(2s^2) \sigma^*(2s^2) \sigma 2p_z^2 \pi(2p_y^2) \pi(2p_x^2)$	$\frac{8-2}{2} = 3$
O ₂	$KK\sigma(2s^2) \sigma^*(2s^2) \sigma(2p_z^2) \pi(2p_y^2) \pi(2p_x^2) \pi^*(2p_y^1) \pi^*(2p_x^1)$	$\frac{8-4}{2} = 2$
O ₂ ⁺	$KK\sigma(2s^2) \sigma^*(2s^2) \sigma(2p_z^2) \pi(2p_y^2) \pi(2p_x^2) \pi^*(2p_y^1)$	$\frac{8-3}{2} = 2.5$
O ₂ ⁻	$KK\sigma(2s^2) \sigma^*(2s^2) \sigma(2p_z^2) \pi(2p_y^2) \pi(2p_x^2) \pi^*(2p_y^2) \pi^*(2p_x^1)$	$\frac{8-5}{2} = 1.5$
O ₂ ²⁻	$KK\sigma(2s^2) \sigma^*(2s^2) \sigma(2p_z^2) \pi(2p_y^2) \pi(2p_x^2) \pi^*(2p_y^2) \pi^*(2p_x^2)$	$\frac{8-6}{2} = 1$
F ₂	$KK\sigma(2s^2) \sigma^*(2s^2) \sigma(2p_z^2) \pi(2p_y^2) \pi(2p_x^2) \pi^*(2p_y^2) \pi^*(2p_x^2)$	$\frac{8-6}{2} = 1$
Ne ₂	$KK\sigma(2s^2) \sigma^*(2s^2) \sigma(2p_z^2) \pi(2p_y^2) \pi(2p_x^2) \pi^*(2p_y^2) \pi^*(2p_x^2) \pi^*(2p_z^2)$	$\frac{8-8}{2} = 0$
NO	$KK\sigma(2s^2) \sigma^*(2s^2) \sigma(2p_z^2) \pi(2p_y^2) \pi(2p_x^2) \pi^* 2p_y^1$	$\frac{8-3}{2} = 2.5$
CO	$KK\sigma(2s^2) \sigma^*(2s^2) \sigma(2p_z^2) \pi(2p_y^2) \pi(2p_x^2)$	$\frac{8-2}{2} = 3$

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. Write the electronic configuration of O₂²⁻ molecule on the basis of M.O. Theory and calculate its bond order.

SOLUTION : (i) Electronic Configuration



(ii) To calculate bond order

Formula used

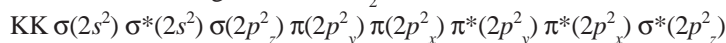
$$\text{Bond order} = \frac{N_b - N_a}{2}$$

$$N_b = 8$$

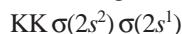
$$N_a = 6$$

Substitution of values

$$\text{Bond order} = \frac{8-6}{2} = 1$$

SOLVED PROBLEM 2. Why does the molecule Ne_2 not exist ?**SOLUTION :** Two electronic configuration of Ne_2 molecule is

$$\begin{aligned} \text{Bond order} &= \frac{N_b - N_a}{2} \\ &= \frac{8-8}{2} \\ &= 0 \end{aligned}$$

Since the bond order in Ne_2 is zero, it does not exist.**SOLVED PROBLEM 3.** Calculate the bond order in He^+ on the basis of M.O. theory.**SOLUTION :** The electronic configuration of He^+ is

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2-1}{2} = 0.5$$

ADDITIONAL PRACTICE PROBLEMS

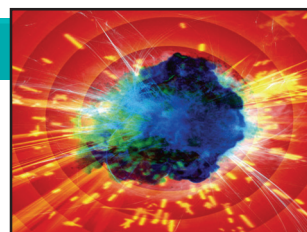
- The O–O bond length in O_2^+ is 1.12\AA and in O_2 is 1.21\AA . Explain why the bond length in O_2^+ is shorter than O_2 .
- Write the molecular orbital configuration of C_2^{2-} and calculate the bond order of the acetylide in C_2^{2-} .
Answer. Three
- Write the molecular orbital configuration of O_2^- ion.
Answer. $\text{KK } \sigma(2s^2) \sigma^*(2s^2) \sigma(2p_z^2) \pi(2p_y^2) \pi(2p_x^2) \pi^*(2p_y^2) \pi^*(2p_x^1)$
- Write MO configuration for O_2 and O_2^{2-} and which of them is paramagnetic ?
Answer. O_2 is paramagnetic
- On the basis of bond order, predict which of the following species is the most stable?
 O_2^- O_2 and Ne_2^+
Answer. O_2 is most stable
- Write the ground state electronic configuration of O_2^+ on the basis of MO theory.
Answer. $\text{KK } \sigma(2s^2) \sigma^*(2s^2) \sigma(2p_z^2) \pi(2p_y^2) \pi(2p_x^2) \pi^*(2p_x^1)$
- Which has greater bond dissociation energy N_2 or N_2^+ ?
Answer. N_2 , as it has bond order of three.
- Write the electronic configuration of Be_2 molecule and calculate its bond order.
Answer. $\text{KK } \sigma(2s^2) \sigma^*(2s^2)$; zero
- Write the ground state electronic configuration of N_2^- on the basis of MO theory and calculate its bond order.
Answer. $\text{KK } \sigma(2s^2) \sigma^*(2s^2) \sigma(2p_z^2) \pi(2p_y^2) \pi(2p_x^2) \pi^*(2p_y^1)$; 2.5
- Calculate the number of antibonding electrons in O_2^{2-} molecule on the basis of M.O. theory.
Answer. Four

7

First Law of Thermodynamics

CHAPTER

KEY CONCEPTS AND EQUATIONS



THERMODYNAMICS

The study of the flow of heat or any other form of energy into or out of a system as it undergoes a physical or chemical transformation, is called Thermodynamics.

FIRST LAW OF THERMODYNAMICS

The total energy of an isolated system remains constant though it may change from one form to another, or,

Energy can neither be created nor, destroyed, it can only be converted from one form to other.

MATHEMATICAL STATEMENT OF THE FIRST LAW

$$\Delta E = q - w$$

where ΔE is the change in internal energy, q is the amount of heat supplied to the system and w is the work done by the system.

WORK DONE IN AN ISOTHERMAL REVERSIBLE EXPANSION

The work done in reversible expansion from value V_1 to V_2 at a constant temperature is given by

$$w = -2.303 \times n R T \log \frac{P_1}{P_2}$$

$$\text{or} \quad w = 2.303 \times n R T \log \frac{P_2}{P_1}$$

$$\text{or} \quad = 2.303 \times n R T \log \frac{V_1}{V_2}$$

where P_1 is the initial pressure, P_2 is the final pressure, n the number of moles of the gas, R the gas constant and T the absolute temperature.

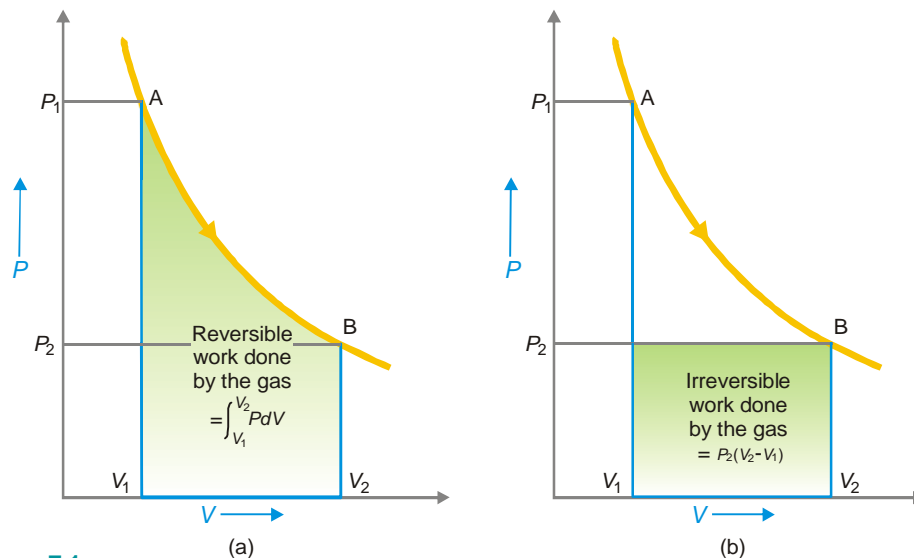
WORK DONE IN AN IRREVERSIBLE EXPANSION

The work done in an irreversible expansion of a gas from volume V_1 to V_2 is given by

$$w = P_2 (V_2 - V_1)$$

where P_2 is the final pressure ; V_1 the initial volume and V_2 the final volume.

It may be noted that work is not a state function as it depends on the path by which the process is performed rather than the initial and final states. Thus, it is path function.



■ Figure 7.1

(a) The reversible work of expansion; (b) The irreversible work done by the gas when the external pressure is at once dropped to the final value P_2 .

INTERNAL ENERGY AND ENTHALPY

The total of all possible kinds of energy of a system is called its Internal Energy. It is a state function and is an extensive property. It is denoted by E .

The total heat content of a system at constant pressure is equivalent to the internal energy E plus the PV energy. This is called the Enthalpy and is defined by the equation.

$$H = E + PV$$

It is state function and is independent of the path. The change in internal energy and enthalpy is denoted by

$$\Delta E = E_2 - E_1$$

and

$$\Delta E = H_2 - H_1$$

where E_1 and H_1 are internal energy and enthalpy in the initial state and E_2 and H_2 are internal energy and the enthalpy in the final state.

RELATION BETWEEN ΔH AND ΔE

$$\Delta H = \Delta E + P \Delta V$$

or

$$\Delta H = \Delta E + \Delta n RT$$

where ΔV is the change in volume ($V_2 - V_1$).

Δn is the change in number of moles of gaseous products and gaseous reactants and is given by $\Delta n = n_2 - n_1$ where n_2 is the no. of moles of gaseous products and n_1 is the no. of moles of gaseous reactants.

MOLAR HEAT CAPACITIES

The molar heat capacity of a system is defined as the amount of heat required to raise the temperature of one mole of the substance (system) by 1 K. It varies with temperature and is given by

$$C = \frac{dq}{dt}$$

where dq is the small quantity of heat absorbed by the system producing a small rise dt . It is also defined as the ratio of the amount of heat absorbed to rise in temperature. It is not a state function.

MOLAR HEAT CAPACITY AT CONSTANT VOLUME

$$C_v = \frac{\Delta E}{T_2 - T_1}$$

where ΔE is the amount of heat absorbed at constant volume. Thus the heat capacity at constant volume is defined as the rate of change of internal energy with temperature at constant volume.

MOLAR HEAT CAPACITY AT CONSTANT PRESSURE

$$C_p = \frac{\Delta H}{T_2 - T_1}$$

where ΔH is the amount of heat absorbed at constant volume. Thus heat capacity at constant pressure is defined as the rate of change of enthalpy with temperature at constant pressure.

RELATION BETWEEN C_p AND C_v

C_p is greater than C_v . These two are related to each other by the relation

$$C_p - C_v = R$$

CALCULATION OF ΔE AND ΔH

$$\begin{aligned} \Delta E &= n \times C_v (T_2 - T_1) \\ \text{and} \quad \Delta H &= n \times C_p (T_2 - T_1) \end{aligned}$$

ADIABATIC EXPANSION OF AN IDEAL GAS

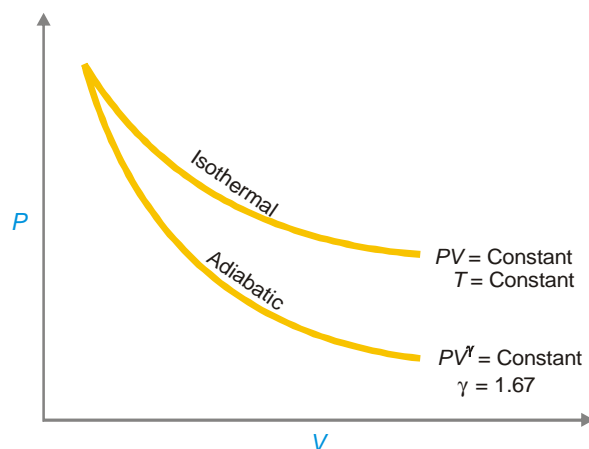
In an adiabatic process there is no heat exchange between a system and surroundings *i.e.* $q = 0$

$$\text{also} \quad \frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma-1} \quad \text{or} \quad TV^{\gamma-1} = \text{a constant}$$

$$\text{and} \quad \frac{P_2}{P_1} = \left(\frac{V_1}{V_2} \right)^{\gamma} \quad \text{or} \quad PV^{\gamma}$$

$$\text{where} \quad \gamma = \frac{C_p}{C_v}$$

In an isothermal process, temperature of system remains constant while in an adiabatic process temperature must change. These two processes are shown in Fig 7.2.



■ Figure 7.2

Curves for isothermal and adiabatic expansions for a monoatomic ideal gas.

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. A dry gas at NTP is expanded adiabatically from 1 litre to 5 litre. Calculate the final temperature and pressure assuming ideal behaviour ($C_p / C_v = 1.4$)

SOLUTION : (a) To calculate the temperature

Formula used

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma-1} \text{ or } T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\gamma-1}$$

Quantities given

$$T_1 = 273 \text{ K}$$

$$V_1 = 1 \text{ litre}$$

$$V_2 = 5 \text{ litres}$$

$$\gamma = 1.4$$

Substitution of values

$$T_2 = 273 \text{ K} \times \left(\frac{1 \text{ litre}}{5 \text{ litre}} \right)^{1.40-1}$$

Taking logarithms

$$\log T_2 = \log 273 + 0.40 \log \frac{1}{5}$$

or

$$= 2.4361 + 0.40(-0.6990)$$

or

$$\begin{aligned} \log T_2 &= 2.4361 - 0.2796 \\ &= 2.1565 \end{aligned}$$

Taking Antilogarithms

$$\begin{aligned} T_2 &= \text{Antilog } 2.1565 \\ &= 143.4 \text{ K} \end{aligned}$$

(ii) To calculate the pressure

Formula used

$$\frac{P_1}{P_2} = \left(\frac{V_2}{V_1} \right)^{\gamma}$$

Quantities given

$$P_1 = 1 \text{ atm}$$

$$V_1 = 1 \text{ litre}$$

$$V_2 = 5 \text{ litres}$$

$$\gamma = 1.4$$

Substitution of values

$$\frac{1 \text{ atm}}{P_2} = \left(\frac{5 \text{ litre}}{1 \text{ litre}} \right)^{1.40}$$

or

$$P_2 = \left(\frac{1}{5} \right)^{1.40} \text{ atm}$$

Taking logarithms

$$\begin{aligned} \log P_2 &= 1.40 \log (0.2) \\ &= 1.40(-0.6990) \\ &= -0.9786 \end{aligned}$$

or

$$\begin{aligned} P_2 &= \text{Antilog } (-0.9786) \\ &= \mathbf{0.1050 \text{ atm}} \end{aligned}$$

SOLVED PROBLEM 2. Calculate the maximum work done when 44 g of Neon gas expands reversibly and isothermally from 10 atm to 2 atm pressure at constant temperature 27 °C. (Neon at. mass = 20; $R = 2 \text{ cal deg}^{-1} \text{ mol}^{-1}$).

SOLUTION :**Formula used**

$$w = 2.303 \times n R T \log \frac{P_1}{P_2}$$

Quantities given

$$n = \frac{44}{20} = 2.2 \text{ moles}$$

$$R = 2 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

$$T = 27 + 273 = 300 \text{ K}$$

$$P_1 = 10 \text{ atm}$$

$$P_2 = 2 \text{ atm}$$

Substitution of values

$$\begin{aligned} w &= 2.303 \times 2.2 \text{ mol} \times 2 \text{ cal K}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \times \log \frac{10 \text{ atm}}{2 \text{ atm}} \\ &= 3039.96 \text{ cal} \times \log 5 \\ &= \mathbf{2124.84 \text{ cal}} \end{aligned}$$

SOLVED PROBLEM 3. How many calories of heat are required to heat 1 mole of Argon from 40 °C to 100 °C at (i) Constant Volume and (ii) at Constant pressure ?

Molar heat capacity of Ar at constant volume = 3 cal K⁻¹

Molar heat capacity of Ar at constant pressure = 5 cal K⁻¹

Solution : (i) At constant volume**Formula used**

$$\Delta E = n \times C_v \times (T_2 - T_1)$$

Quantities given

$$n = 1 \text{ mole}$$

$$C_v = 3 \text{ cal K}^{-1}$$

$$T_2 = 100 + 273 = 373 \text{ K}$$

$$T_1 = 40 + 273 = 313 \text{ K}$$

Substitution of values

$$\begin{aligned} \Delta E &= 1 \times 3 \times (373 - 313) \text{ cal} \\ &= \mathbf{180 \text{ cal}} \end{aligned}$$

(ii) At constant pressure**Formula used**

$$\Delta H = n \times C_p \times (T_2 - T_1)$$

Quantities given

$$n = 1 \text{ mole}$$

$$C_p = 5 \text{ cal K}^{-1}$$

$$T_2 = 373 \text{ K}$$

$$T_1 = 313 \text{ K}$$

Substitution of values

$$\begin{aligned} \Delta H &= 1 \times 5 \times (373 - 313) \\ &= \mathbf{300 \text{ cal}} \end{aligned}$$

SOLVED PROBLEM 4. Calculate the work of expansion of one mole of an ideal gas at 25 °C under isothermal conditions, the pressure being changed from 1 atm to 5 atm.

SOLUTION :**Formula used**

$$w = 2.303 \times n R T \log \frac{P_1}{P_2}$$

Quantities given

$$n = 1 \text{ mole}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T = 25 + 273 = 298 \text{ K}$$

$$P_1 = 1 \text{ atm}$$

Substitution of values

$$\begin{aligned} w &= 2.303 \times 1 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \log \frac{1 \text{ atm}}{5 \text{ atm}} \\ &= 5705.848 \times \log \frac{1}{5} \\ &= 5705.848 \times (0.6990) \\ &= -3988.38 \text{ J} \end{aligned}$$

$$P_2 = 5 \text{ atm}$$

SOLVED PROBLEM 5. Calculate the value of ΔE and ΔH on heating 64.0 grams of oxygen from 0°C to 100°C . C_v and C_p on an average are 5.0 and $7.0 \text{ cal mol}^{-1} \text{ deg}^{-1}$ respectively.

SOLUTION : (i) To calculate ΔE

Formula used

$$\Delta E = n \times C_v \times (T_2 - T_1)$$

Quantities given

$$n = \frac{64 \text{ g}}{32 \text{ g mol}^{-1}} = 2 \text{ mol}$$

$$C_v = 5 \text{ cal K mol}^{-1}$$

$$T_2 = 100 + 273 = 373 \text{ K}$$

$$T_1 = 273 \text{ K}$$

Substitution of values

$$\begin{aligned} \Delta E &= 2 \text{ mol} \times 5 \text{ cal K}^{-1} \text{ mol}^{-1} \times (373 \text{ K} - 273 \text{ K}) \\ &= 10 \times 100 \text{ cal} \\ &= 1000 \text{ cal} \end{aligned}$$

(i) To calculate ΔH

Formula used

$$\Delta H = n \times C_p \times (T_2 - T_1)$$

Quantities given

$$n = 2 \text{ mol}$$

$$C_p = 7 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$T_2 = 373 \text{ K}$$

$$T_1 = 273 \text{ K}$$

Substitution of values

$$\begin{aligned} \Delta H &= 2 \text{ mol} \times 7 \text{ cal K}^{-1} \text{ mol}^{-1} \times (373 \text{ K} - 273 \text{ K}) \\ &= 14 \times 100 \text{ cal} \\ &= 1400 \text{ cal} \end{aligned}$$

SOLVED PROBLEM 6. One mole of an ideal gas expands isothermally and reversibly from 1 litre to 100 litres at 27°C . Calculate w , q , ΔE , ΔH and ΔS for the process.

SOLUTION : (i) To calculate w

Formula used

$$w = 2.303 n R T \times \log \frac{V_2}{V_1}$$

Quantities given

$$n = 1 \text{ mol}$$

$$T = 300 \text{ K}$$

$$V_2 = 100 \text{ litres}$$

$$V_1 = 1 \text{ litre}$$

$$R = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$$

Substitution of values

$$\begin{aligned} w &= 2.303 \times 1 \text{ mol} \times 1.987 \text{ cal K}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \times \log \frac{100 \text{ litre}}{1 \text{ litre}} \\ &= 1372.818 \text{ cal} \times \log 100 \\ &= 2745.637 \text{ cal} \end{aligned}$$

(ii) To calculate q and ΔE

Formula used

$$\Delta E = q - w = 0$$

or

$$q = w$$

 \therefore

$$q = 2745.636 \text{ cal} \quad \text{and} \quad \Delta E = 0$$

(iii) To calculate ΔH **Formula used**

$$\Delta H = \Delta E + \Delta n (R T)$$

Quantities given

$$\Delta E = 0$$

$$\Delta n = 1$$

$$R = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$T = 300 \text{ K}$$

Substitution of values

$$\begin{aligned} \Delta H &= 0 + 1 \text{ mol} \times 1.987 \text{ cal K}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \\ &= \mathbf{596.1 \text{ cal}} \end{aligned}$$

(iv) To calculate ΔS **Formula used**

$$\Delta S = \frac{q}{T}$$

Quantities given

$$q = 2745.636 \text{ cal}$$

$$T = 300 \text{ K}$$

Substitution of values

$$\begin{aligned} \Delta S &= \frac{2745.636 \text{ cal}}{300 \text{ K}} \\ &= \mathbf{9.152 \text{ cal K}^{-1}} \end{aligned}$$

SOLVED PROBLEM 7. Calculate the maximum work obtained when 2 moles of nitrogen were expanded isothermally and reversibly from 10 litres to 20 litres at 25 °C.

SOLUTION :**Formula used**

$$w = 2.303 n R T \log \frac{V_2}{V_1}$$

Quantities given

$$n = 2 \text{ mol}$$

$$T = 298 \text{ K}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$V_1 = 10 \text{ litres}$$

$$V_2 = 20 \text{ litres}$$

Substitution of values

$$\begin{aligned} w &= 2.303 \times 2 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \log \frac{20 \text{ litre}}{10 \text{ litre}} \\ &= 11411.69 \text{ cal} \times \log 2 \\ &= 11411.69 \text{ cal} \times 0.3010 \\ &= \mathbf{3434.92 \text{ J}} \end{aligned}$$

SOLVED PROBLEM 8. Calculate ΔE and ΔH when the temperature of one mole of water is increased from 10 °C to 70 °C. The density of water is 0.9778 g cm⁻³ and 0.9997 g cm⁻³ at 70 °C and 10 °C respectively.

SOLUTION : (i) To calculate ΔH **Formula used**

$$\Delta H = n \times C_p \times (T_2 - T_1)$$

Quantities given

$$n = 1 \text{ mole}$$

$$C_p = 18 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$T_2 = 70 + 273 = 343 \text{ K}$$

$$T_1 = 10 + 273 = 283 \text{ K}$$

Substitution of values

$$\begin{aligned} \Delta H &= 1 \text{ mol} \times 18 \text{ cal K}^{-1} \text{ mol}^{-1} \times (343 \text{ K} - 283 \text{ K}) \quad [\because C_p = 18 \text{ cal K}^{-1} \text{ as its sp heat} = 1] \\ &= \mathbf{1080 \text{ cal} = 1080 \text{ cal}} \end{aligned}$$

(ii) To calculate ΔE **Formula used**

$$\Delta E = \Delta H - P(V_2 - V_1)$$

Quantities given

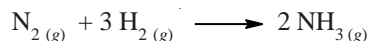
$$V_1 = \frac{18 \times 24.2}{0.9997 \times 1000} = \frac{18 \times 24.2}{1000} \left[\frac{1}{0.9997} \right] \quad \left[\because \text{Molar Vol.} = \frac{\text{Mol. mass}}{\text{Density}} \right]$$

$$V_2 = \frac{18 \times 24.2}{0.9778 \times 1000} = \frac{18 \times 24.2}{1000} \left[\frac{1}{0.9778} \right]$$

$$\Delta H = 1080 \text{ cal}$$

Substitution of values

$$\begin{aligned} \Delta E &= 1080 \text{ cal} - \frac{24.2 \times 18}{1000} \left[\frac{1}{0.9778} - \frac{1}{0.9997} \right] \text{ cal} \\ &= 1080 \text{ cal} - 0.4356 \times (0.02240) \text{ cal} \\ &= 1080 - 0.009757 \text{ cal} \\ &= 1079.99 \text{ cal} \end{aligned}$$

SOLVED PROBLEM 9. Calculate ΔE for the following process, for which $q = -93.78 \text{ kJ}$ at STP**SOLUTION : (i) To calculate the work done in the process****Formula used**

$$w = P \Delta V = \Delta n R T$$

Quantities given

$$\Delta n = n_p - n_R = 2 \text{ moles} - 4 \text{ moles} = -2 \text{ moles} \quad R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \quad T = 273 \text{ K}$$

Substitution of values

$$\begin{aligned} w &= -2 \text{ moles} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 273 \text{ K} \\ &= -4539.44 \text{ J} \\ &= -4.53944 \text{ kJ} \end{aligned}$$

(ii) To calculate the value of ΔE **Formula given**

$$\Delta E = q - w$$

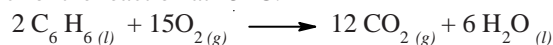
Quantities given

$$q = -93.78 \text{ kJ}$$

$$w = -4.5394 \text{ kJ}$$

Substitution of values

$$\begin{aligned} \Delta E &= -93.78 \text{ kJ} - (-4.53944 \text{ kJ}) \\ &= -89.240 \text{ kJ} \end{aligned}$$

SOLVED PROBLEM 10. Calculate the difference between heats of reaction at constant pressure and constant volume in kJ for the reaction at 25°C .**SOLUTION :****Formula used**

$$\Delta H = \Delta E + \Delta n R T$$

or

$$\Delta H - \Delta E = \Delta n R T$$

Quantities given

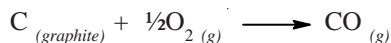
$$\Delta n = n_p - n_R = 12 - 15 = -3 \text{ moles}$$

[\because C_6H_6 and H_2O are in liquid state]

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \quad T = 298 \text{ K}$$

Substitution of values

$$\begin{aligned} \Delta H - \Delta E &= -3 \text{ mole} \times 8.314 \text{ JK}^{-1} \text{ mole}^{-1} \times 298 \text{ K} \\ &= -7432.7 \text{ J} \\ &= -7.4327 \text{ kJ} \end{aligned}$$

SOLVED PROBLEM 11. For the reaction

at 298 K and 1 atm pressure, $\Delta H = -110.60 \text{ kJ}$. Calculate ΔE if the molar volume of graphite is 0.0053 litres, assuming ideal conditions.

SOLUTION :**Formula used**

$$\Delta H = \Delta E + \Delta n R T$$

Quantities given

$$\Delta H = -110.60 \text{ kJ}$$

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1} = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$T = 298 \text{ K}$$

$$\Delta n = n_p - n_R = 1 - \frac{1}{2} = \frac{1}{2} \text{ mole (neglecting the molar volume of graphite)}$$

Substitution of values

$$\begin{aligned} -110.60 \text{ kJ} &= \Delta E + \frac{1}{2} \text{ mole} \times 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \\ &= \Delta E + 1.238 \text{ kJ} \\ \Delta E &= -110.60 \text{ kJ} - 1.238 \text{ kJ} \\ &= -111.838 \text{ kJ} \end{aligned}$$

SOLVED PROBLEM 12. What is the maximum work obtainable from the isothermal expansion of 3 moles of an ideal gas at 27 °C from a pressure of 4 atm to 1 atm. Also calculate the quantity of heat evolved in the process.

SOLUTION :**(i) To calculate the maximum work obtainable****Formula used**

$$w_{\max} = 2.303 \times n R T \log \frac{P_1}{P_2}$$

Quantities given

$$n = 3 \text{ moles}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T = 27 + 273 = 300 \text{ K}$$

$$P_1 = 4 \text{ atm}$$

$$P_2 = 1 \text{ atm}$$

Substitution of values

$$\begin{aligned} w_{\max} &= 2.303 \times 3 \text{ moles} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \\ &= 17.232 \text{ kJ} \end{aligned}$$

(ii) To calculate the quantity of heat absorbed**Formula used**

$$\begin{aligned} q &= w_{\max} \\ \therefore q &= 17.232 \text{ kJ} \end{aligned}$$

SOLVED PROBLEM 13. Five moles of a perfect gas with $C_v = 5.0 \text{ cal mole}^{-1} \text{ K}^{-1}$ are compressed adiabatically and reversibly from a volume of 50 litres at 1 atm to a pressure of 100 atm. Calculate (i) the final volume of the gas (ii) the final temperature of the gas.

SOLUTION : (i) To calculate the final volume of the gas

Formula used

$$P_1 V_1^\gamma = P_2 V_2^\gamma$$

$$\text{or} \quad \frac{P_1}{P_2} = \left(\frac{V_2}{V_1} \right)^\gamma$$

Quantities given

$$P_1 = 1 \text{ atm} \quad P_2 = 100 \text{ atm} \quad V_1 = 50 \text{ litres}$$

$$\gamma = \frac{C_p}{C_v} = \frac{C_v + R}{C_v} = \frac{5 + 2}{5} = \frac{7}{5} = 1.4$$

Substitution of values

$$\frac{1 \text{ atm}}{100 \text{ atm}} = \left(\frac{V_2}{50 \text{ lit}} \right)^{1.4}$$

or

$$\frac{1}{100} = \left(\frac{V_2}{50 \text{ lit}} \right)^{1.4}$$

Taking logarithms

$$\log \frac{1}{100} = 1.4 (\log V_2 - \log 50)$$

$$-2 = 1.4 (\log V_2 - 1.6990)$$

$$\frac{-2}{1.4} = \log V_2 - 1.6990$$

or

$$1.6990 - 1.4285 = \log V_2$$

or

$$V_2 = \text{Antilog } 0.2705$$

$$= \mathbf{1.86 \text{ litre}}$$

(ii) Calculate the final temperature of the gas

Formula used

$$P_2 V_2 = n R T_2$$

$$\text{or} \quad T_2 = \frac{P_2 V_2}{n R}$$

Quantities given

$$n = 5 \text{ moles} \quad P_2 = 100 \text{ atm} \quad R = 0.082 \text{ atm lit}^{-1} \text{ K}^{-1} \text{ mol}^{-1} \quad V_2 = 1.86 \text{ litre}$$

Substitution of values

$$T_2 = \frac{100 \text{ atm} \times 1.86 \text{ lit}}{5 \text{ mole} \times 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1}}$$

$$= \mathbf{453 \text{ K}}$$

SOLVED PROBLEM 14. Certain quantity of air at 27°C was allowed to expand adiabatically and reversibly from 100 atm. to 20 atm. Assuming the ideal behaviour, calculate the final temperature of the air ($C_v = 5.0 \text{ cal K}^{-1} \text{ mol}^{-1}$)

SOLUTION :

Formula used

$$\frac{T_2}{T_1} = \left(\frac{P_1}{P_2} \right)^{\frac{1-\gamma}{\gamma}}$$

Quantities given

$$T_1 = 27 + 273 = 300 \text{ K}$$

$$P_1 = 100 \text{ atm}$$

$$P_2 = 20 \text{ atm}$$

$$\gamma = \frac{C_p}{C_v} = \frac{C_v + R}{C_v} = \frac{5 + 2 \text{ cal}}{5 \text{ cal}} = 1.4 \quad \text{and}$$

$$1 - \gamma = 1 - 1.4 = -0.4$$

Substitution of values

$$\frac{T_2}{300 \text{ K}} = \left(\frac{100 \text{ atm}}{20 \text{ atm}} \right)^{\frac{-0.4}{1.4}}$$

$$\text{or} \quad T_2 = 300 \text{ K} \times (5)^{\frac{-0.4}{1.4}}$$

Taking logarithms

$$\begin{aligned} \log T_2 &= \log 300 - \left(\frac{0.4}{1.4} \right) \log 5 \\ &= 2.4771 - 0.2857 \times 0.6990 \\ &= 2.4471 - 0.1997 \end{aligned}$$

$$\begin{aligned} \text{or} \quad T_2 &= \text{Antilog } 2.247 \\ &= 177.4 \text{ K} = 177.4 \text{ K} - 273 = -95.6^\circ \text{C} \end{aligned}$$

ADDITIONAL PRACTICE PROBLEMS

- The internal energy of a system was increased by 400 kJ while the system performed 125 kJ of work on the surroundings. How much heat was transferred between the system and its surrounding during this process ? In what direction did the heat flow ?
Answer. + 525 kJ ; From surroundings to system
- In a certain chemical reaction, 20.6 kcal of heat are evolved. The volume of the reactants is 36.0 litres ; the volume of products is 9.0 litres. What is ΔE for the reaction ?
Answer. - 19.94 kcal
- When one mole of liquid Br_2 is converted to Br_2 vapour at 25°C and 1 atm pressure, 7.3 kcal of heat is absorbed and 0.59 kcal of expansion work is done by the system. Calculate ΔE for this process.
Answer. + 6.7 kcal
- The volume of a certain reaction undergoes a change from 11.2 litre to 33.6 litre during a chemical change taking place at 1.0 atm pressure. If ΔE for the reaction is 12.0 kcal, calculate ΔH for the process ?
Answer. 12.50 kcal
- What is the maximum work which can be obtained by the isothermal reversible expansion of two moles to three moles of an ideal gas at 273 K from 1.12 litre to 11.2 litres ?
Answer. 1627.35 cal
- Calculate w and ΔE for the conversion of 1 mole of water into 1 mole of steam at a temperature of 373 K and 1 atm pressure. Latent heat of vapourisation of water 540 cal g^{-1} .
Answer. 8.979 kcal
- Calculate the maximum work done when pressure of 12 g of hydrogen is reduced from 10 to 1 atm at a constant temperature of 273 K. Assuming that gas behaves ideally. Also calculate ' q '.
Answer. 7495 cal ; 7495 cal

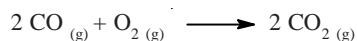
8. Calculate the work done when 5 moles of hydrogen gas expand isothermally and reversibly at 298 K from 10 to 50 litres.

Answer. 4.766 kcal

9. Find the work done when 2 moles of an ideal gas expand isothermally from 2 litres to 5 litres against a constant pressure of 1 atm at 298 K.

Answer. 1085 cal

10. ΔE for the process



is -134.8 kcal at 298 K and 1 atm pressure. What is ΔH for this reaction ?

Answer. 135.4 kcal]

11. Calculate ΔE for the combustion of one mole of Magnesium in an open container at 298 K and 1 atm pressure, if $\Delta H_{\text{combustion}} = -143.9$ kcal ?

Answer. -143.6 kcal

12. 10 g of Argon is compressed isothermally and reversibly at a temperature of 27 °C from 10 litre to 5 litre. Calculate q , w , ΔE and ΔH for this process. $R = 2.0 \text{ cal K}^{-1} \text{ mol}^{-1}$; $\log 2 = 0.30$. At wt. of Ar = 40

Answer. 0 ; 103.6 cal ; -103.6 ; 0

8

Thermochemistry

CHAPTER

KEY CONCEPTS AND EQUATIONS



THERMOCHEMISTRY

It is that branch of Chemistry which deals with the thermal or heat changes caused by Chemical reactions.

CHANGE IN INTERNAL ENERGY, ΔE

The difference of internal energy of the products E_p and that of reactants E_R is change in internal energy denoted by ΔE i.e.

$$\begin{aligned}\Delta E &= E_{\text{Products}} - E_{\text{Reactants}} \\ &= E_p - E_R\end{aligned}$$

If ΔE is + ve then the reaction is Exothermic and if ΔE is – ve then the reaction is Endothermic.

ENTHALPY OF A REACTION

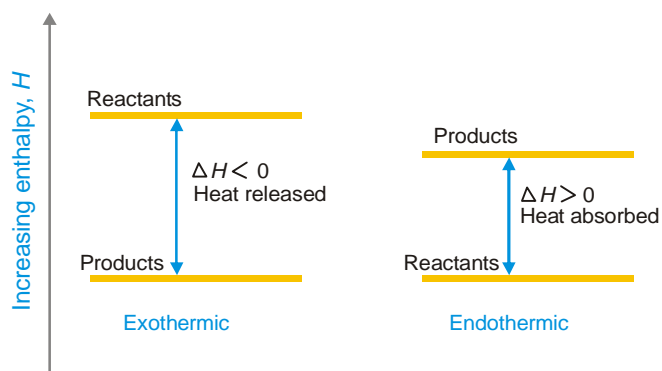
The sum of Internal energy and the product of pressure and volume is called Enthalpy, denoted by H . That is

$$H = E + PV$$

The change in enthalpy, ΔH , is given by the expression

$$\begin{aligned}\Delta H &= H_{\text{Products}} - H_{\text{Reactants}} \\ &= H_p - H_R\end{aligned}$$

For an exothermic reaction ΔH is – ve and $H_p < H_R$ and for an endothermic reaction ΔH is + ve and $H_p > H_R$. It has been illustrated in Fig. 8.1



■ **Figure 8.1**
Enthalpy diagram for an exothermic and endothermic reaction.

RELATION BETWEEN ΔH AND ΔE

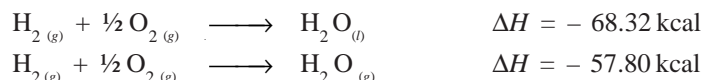
ΔH and ΔE are related to each other by the relation

$$\Delta H = \Delta E + \Delta n R T$$

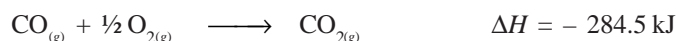
where Δn is the difference of the number of moles of gaseous products and gaseous reactants.

THERMOCHEMICAL EQUATIONS

An equation which indicates the amount of heat change (evolved or absorbed) in the reaction or process is called a Thermochemical equation. For example,

**HEAT OF REACTION AND STANDARD HEAT OF REACTION**

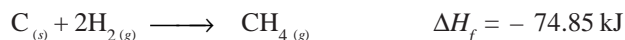
Heat of a reaction may be defined as the amount of heat absorbed or evolved in a reaction when the number of moles of reactants as represented by the balanced chemical equation change completely into the products. It is denoted by ΔH e.g.



The heat change accompanying a reaction taking place at 298 K and one atmosphere pressure is called the **standard heat change** or **standard enthalpy change**. It is denoted by ΔH° e.g.

**DIFFERENT TYPES OF HEAT (ENTHALPY) OF REACTIONS****HEAT OF FORMATION**

The change in enthalpy that takes place when one mole of a compound is formed from its elements. It is denoted by ΔH_f e.g.



By convention the standard heat of formation of all elements is assumed to be zero.

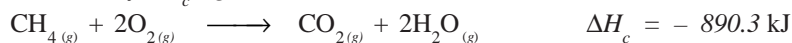
STANDARD HEAT OF FORMATION

It is equal to the standard heat of formation of products minus the standard heat of formation of reactants i.e.

$$\Delta H^\circ = \Delta H^\circ_{f(\text{Products})} - \Delta H^\circ_{f(\text{Reactants})}$$

HEAT OF COMBUSTION

The change in enthalpy of a system when one mole of the substance is completely burnt in excess of air oxygen. It is denoted by ΔH_c e.g.



It may be noted that heat of combustion of a substance is always negative.

HEAT OF SOLUTION

The change in enthalpy when one mole of a substance is dissolved in a solvent so that further dissolution does not give any change in enthalpy. For example,

**HEAT OF NEUTRALISATION**

The change in enthalpy of the system when one gram equivalent of an acid is neutralised by one gram equivalent of base or vice versa in dilute solution. For example,

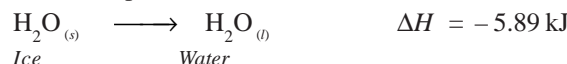


It may be noted that heat of neutralisation of a strong acid and strong base is -57.3 kJ , no matter which acid or base is employed. In fact the heat of neutralisation of an acid and a base is merely the heat of formation of water from hydrogen and hydroxide ions.



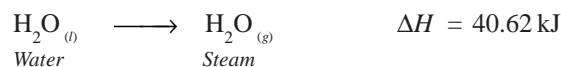
ENERGY CHANGES DURING TRANSITION OR PHASE CHANGES, HEAT OF FUSION

The heat change when one mole of a solid substance is converted into the liquid state at its melting point is called heat of fusion. For example,



HEAT OF VAPORISATION

It is defined as the heat change when one mole of a liquid is converted into vapour or gaseous state at its boiling point. For example,



HEAT OF SUBLIMATION

It is defined as the heat change when one mole of an element changes from one allotropic form to another. For example,



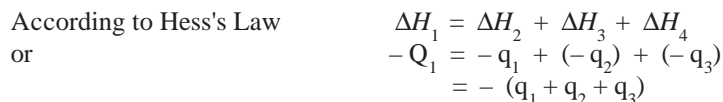
HEAT OF TRANSITION

It is defined as the heat change when one mole of an element changes from one allotropic form to another. For example,



HESS'S LAW OF CONSTANT HEAT SUMMATION

This law states that at constant pressure the total heat change accompanying a chemical reaction is the same no matter by which method the change is brought about. For example,

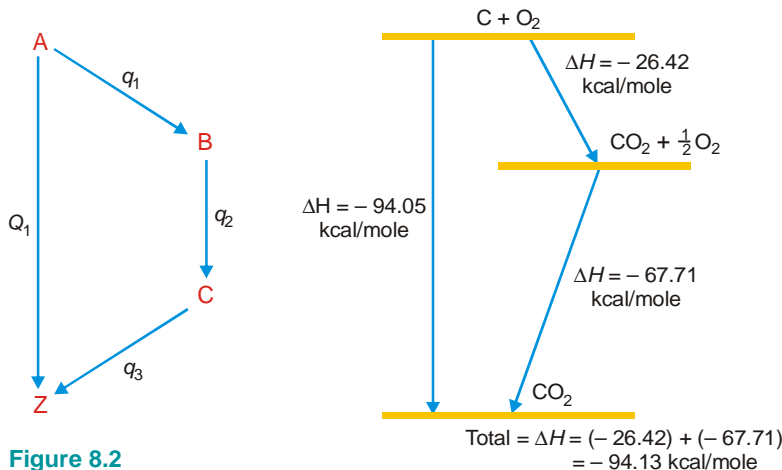


This is shown in the Fig. 8.2 in which the example of formation of CO_2 by two methods has been illustrated. It may be noted that thermochemical equations may be multiplied, added or subtracted like ordinary algebraic equations.

BOND ENERGY

The bond energy is defined as the average of energy required to break all bonds of a particular type in one mole of the substance. It is always positive as heat is always given to the system *e.g.*





■ **Figure 8.2**
Illustration of Hess's Law.

Bond energy is a measure of strength of the bond.

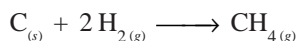
Bond energy data can be used to calculate the heat of the reaction. The energy of formation of a bond is numerically equal to its bond energy with a negative sign.

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. If the heat of formation of methane at constant pressure is $-17.9 \text{ kcal per mole}$ at 25°C , what is its value at constant volume?

SOLUTION :

The equation is



Formula used

$$\Delta H = \Delta E + \Delta n R T$$

Quantities gives

$$\Delta H = -17.9 \text{ kcal mol}^{-1} \quad T = 25 + 273 = 298 \text{ K}$$

$$\Delta N = n_p - n_R = 1 - 2 = -1$$

$$R = 1.987 \text{ cal mol}^{-1} \text{K}^{-1} = 1.987 \times 10^{-3} \text{ kcal mol}^{-1} \text{K}^{-1}$$

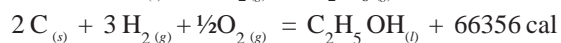
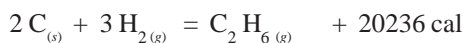
Substitution of values

$$-17.9 \text{ kcal} = \Delta E + (-1) \text{ mol} \times 1.987 \times 10^{-3} \text{ kcal K}^{-1} \text{mol}^{-1} \times 298 \text{ K}$$

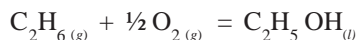
$$\text{or} \quad \Delta E = -17.9 \text{ kcal} + 0.592 \text{ kcal}$$

$$= -17.308 \text{ kcal}$$

SOLVED PROBLEM 2. From the following heats of formation

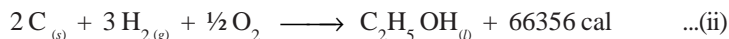
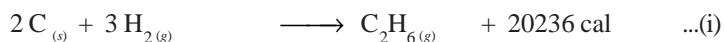


Calculate ΔH for the reaction

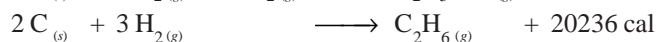
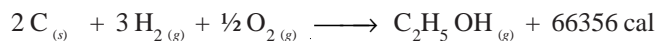


SOLUTION :

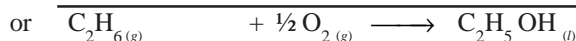
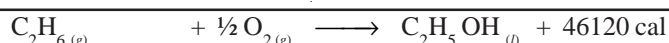
Given equation are



Subtracting (i) from (ii) we have

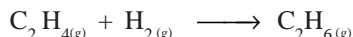


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$$\Delta H = -46120 \text{ cal}$$

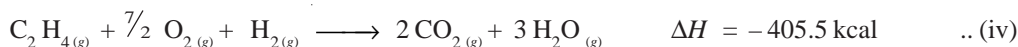
SOLVED PROBLEM 3. Given the heat of combustion of ethylene, hydrogen and ethane are 337.2, 68.3 and 372.8 kcal respectively, calculate the heat of the reaction at 78 °C for

**SOLUTION :**

From the given data we can frame the following equations



Adding (i) and (ii) we get



Subtracting (iii) from (iv) we have



— — — — —



SOLVED PROBLEM 4. Heats of solution of hydrated copper sulphate and anhydrous copper sulphate are -2.80 and 15.89 kcal respectively. Calculate the heat of hydration of copper sulphate.

SOLUTION :

Heat of hydration = Heat of hydration of hydrated salt - Heat of hydration of anhydrous salt

$$\Delta H_{\text{Hydration}} = \Delta H_{\text{Sol}} \text{ of hydrated } \text{CuSO}_4 \cdot 5\text{H}_2\text{O} - \Delta H_{\text{Sol}} \text{ of } \text{CuSO}_4$$

Quantities given

$$\Delta H_{\text{Sol}} \text{ of } \text{CuSO}_4 \cdot 5\text{H}_2\text{O} = -2.80 \text{ kcal}$$

$$\Delta H_{\text{Sol}} \text{ of } \text{CuSO}_4 = 15.89 \text{ kcal}$$

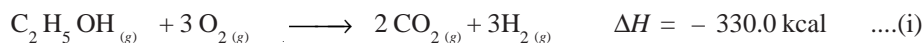
Substitution of values

$$\begin{aligned} \Delta H_{\text{Hydration}} &= -2.80 \text{ kcal} - 15.89 \text{ kcal} \\ &= -18.69 \text{ kcal} \end{aligned}$$

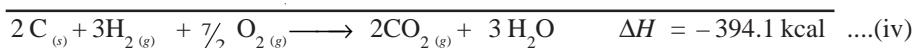
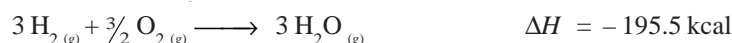
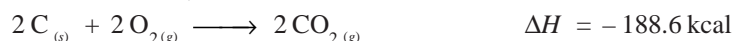
SOLVED PROBLEM 5. ΔH for the combustion of ethyl alcohol, carbon and hydrogen are -330.0 , -94.3 and -68.5 kcal respectively. Calculate the heat of formation of ethyl alcohol.

SOLUTION :

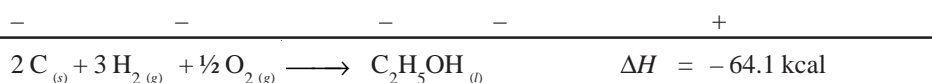
From the given data we can frame the following equations



Multiplying equation (ii) by 2 and (iii) by 3 and adding we have



Subtracting equation (i) from (iv) we have

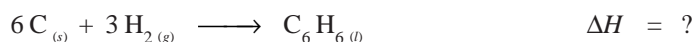


Thus the heat of combustion of ethyl alcohol = -64.1 kcal

SOLVED PROBLEM 6. Calculate the heat of formation of benzene at 25°C , if the heats of combustion of benzene, carbon and hydrogen are -780.90 , 94.05 and -68.32 kcal respectively at 25°C .

SOLUTION :

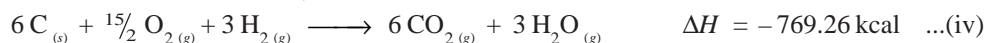
The formation of benzene is represented by



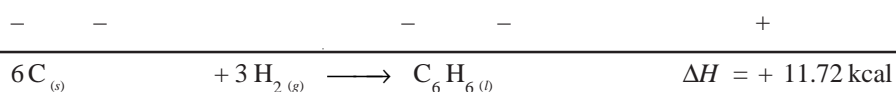
From the given data we can frame the following equations



Multiplying equation (ii) by 6 and (iii) by 3 and adding we get

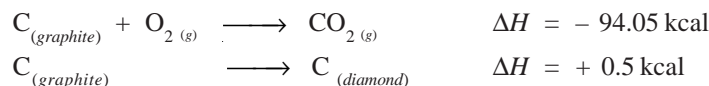


Subtracting (i) from (iv), we have



Thus the heat of formation benzene = $+11.72$ kcal

SOLVED PROBLEM 7. Given following thermochemical equations :

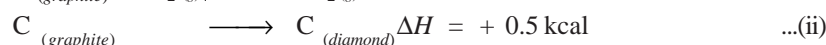


Calculate (i) Enthalpy change for burning $\text{C}_{(\text{diamond})}$

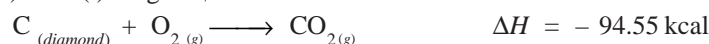
(ii) quantity of $\text{C}_{(\text{graphite})}$ must be burnt to evolve 100 kcal of heat.

SOLUTION : (i) To calculate the enthalpy change

Given that



Subtracting (ii) from (i) we get



Thus the enthalpy change for burning $\text{C}_{(\text{diamond})}$ is -94.55 kcal

(ii) To calculate the quantity of $\text{C}_{(\text{graphite})}$ burnt to evolve 100 kcal of heat

12 g of $\text{C}_{(\text{graphite})}$ burn to give heat = 94.05 kcal

\therefore Amount of $\text{C}_{(\text{graphite})}$ that burns to give 100 kcal of heat

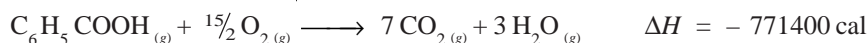
$$= \frac{12 \text{ g} \times 100 \text{ kcal}}{94.05 \text{ kcal}}$$

$$= 12.759 \text{ g}$$

SOLVED PROBLEM 8. The heat of combustion of benzoic acid at constant pressure is -771400 cal at 25°C . Calculate the heat of combustion at constant volume.

SOLUTION :

The equation representing combustion of benzoic acid is



Formula used

$$\Delta H = \Delta E + \Delta n R T \quad \text{or} \quad \Delta E = \Delta H - \Delta n R T$$

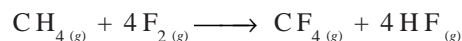
Quantities given

$$\Delta n = n_p - n_r = 7 - \frac{15}{2} = \frac{1}{2} \text{ mol} \quad T = 298 \text{ K} \quad R = 1.987 \text{ cal}^{-1} \text{ mol}^{-1}$$

Substitution of values

$$\begin{aligned} \Delta E &= -771400 \text{ cal} - \left(-\frac{1}{2} \text{ mol} \right) \times 298 \text{ K} \times 1.987 \text{ cal K}^{-1} \text{ mol}^{-1} \\ &= -771400 \text{ cal} + 296.063 \text{ cal} \\ &= -771103.937 \text{ cal} \end{aligned}$$

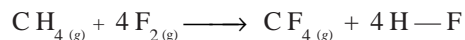
SOLVED PROBLEM 9. Calculate the heat of reaction, ΔH , of the following reaction



Bond energies of C—H, F—F, C—F and H—F bonds are 99.3, 38.0, 116.0 and 135 kcal mol⁻¹ respectively.

SOLUTION :

The heat of the reaction



is given by

$$\begin{aligned}
 \Delta H &= [4 \times \text{Bond energy of (C—F)} + 4 \times (\text{Bond energy of H—F})] - \\
 &\quad [4 \times (\text{Bond energy of C—H}) + 4 \times (\text{Bond energy of F—F})] \\
 &= [4 \times 116.0 + 4 \times 135] - [4 \times 99.3 + 4 \times 38.0] \\
 &= 1004 \text{ kcal} - 549.2 \text{ kcal} \\
 &= \mathbf{454.8 \text{ kcal}}
 \end{aligned}$$

SOLVED PROBLEM 10. The heat of formation of methane at 27 °C is – 19.3 kcal when the measurements are made at constant pressure. What will be the heat of formation at constant volume?

SOLUTION :

Given that



Formula used

$$\Delta H = \Delta E + \Delta n R T \quad \text{or} \quad \Delta E = \Delta H - \Delta n R T$$

Quantities given

$$\Delta H = n_p - n_R = 1 - 2 = -1 \quad R = 1.987 \times 10^{-3} \text{ kcal}$$

Substitution of values

$$\begin{aligned}
 \Delta E &= -19.3 \text{ kcal} - [(-1) \times 1.987 \times 10^{-3} \text{ kcal K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}] \\
 &= -19.3 \text{ kcal} - 0.5961 \text{ kcal} \\
 &= \mathbf{-18.7039 \text{ kcal}}
 \end{aligned}$$

SOLVED PROBLEM 11. Bond energies of F₂ and Cl₂ are 36.6 and 580 kcal mol⁻¹ respectively. Heat liberated in the reaction F₂ + Cl₂ → 2 F Cl is 26.6 kcal. Find the bond energy of F — Cl bond.

SOLUTION :

The given reaction is



The heat of the reaction is given by

$$\Delta H = [2 \times \text{Bond energy of F—Cl}] - [\text{Bond energy of F—F} + \text{Bond energy of Cl—Cl}]$$

Quantities given

$$\Delta H = -26.6 \text{ kcal} \quad \text{B.E. of F—F} = 36.6 \text{ kcal mol}^{-1} \quad \text{B.E. of Cl—Cl} = 580 \text{ kcal mol}^{-1}$$

Substitution of values

$$\begin{aligned}
 -26.6 \text{ kcal} &= [2 \times \text{Bond energy of F—Cl}] - [36.6 \text{ kcal} + 580 \text{ kcal}] \\
 -26.6 \text{ kcal} &= 2 \times \text{Bond energy of F—Cl} - 616.6 \text{ kcal} \\
 \therefore 2 \times \text{Bond energy of F—Cl} &= 616.6 \text{ kcal} - 26.6 \text{ kcal} \\
 \text{Bond of energy of F—Cl} &= \frac{590}{2} \text{ kcal} \\
 &= 295 \text{ kcal}
 \end{aligned}$$

Thus bond energy of F — Cl bond = 295 kcal

SOLVED PROBLEM 12. Graphite and diamond are two forms of carbon. The enthalpy of combustion of graphite at 25 °C is – 393.51 kJ mol⁻¹ and that of diamond is – 395.41 kJ mol⁻¹. What is the enthalpy change in the process graphite → diamond at that temperature?

SOLUTION :

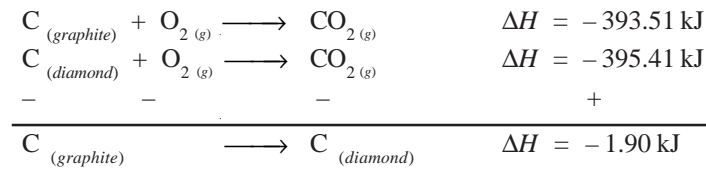
From the given data we can frame the following equations



The required equation is



Subtracting equation (ii) from (i) we have

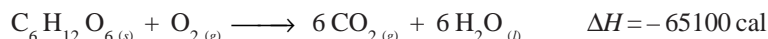


Thus the enthalpy of the process $\text{C}_{(\text{graphite})} \longrightarrow \text{C}_{(\text{diamond})}$ is **+ 1.90 kJ**

SOLVED PROBLEM 13. The heat of combustion of glucose at 17 °C and at constant pressure is – 651000 cal. Calculate heat of combustion at constant volume at 17 °C.

SOLUTION :

The given equation is



Formula used

$$\Delta H = \Delta E + \Delta n R T \quad \text{or} \quad \Delta E = \Delta H - \Delta n R T$$

Quantities given

$$\Delta H = -651000 \text{ cal}$$

$$\Delta n = n_p - n_R = 6 - 6 = 0$$

$$T = 17 + 273 = 290 \text{ K}$$

$$R = 1.987 \text{ cal K}^{-1}\text{mol}^{-1}$$

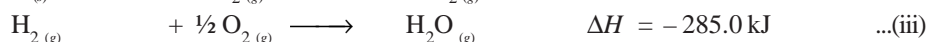
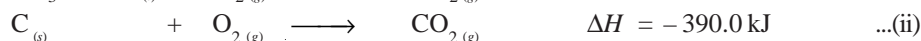
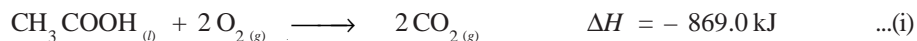
Substitution of values

$$\begin{aligned} \Delta E &= -651000 \text{ cal} - 0 \times 1.987 \text{ cal K}^{-1}\text{mol}^{-1} \times 290 \text{ K} \\ &= -651000 \text{ cal} \end{aligned}$$

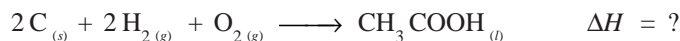
SOLVED PROBLEM 14. Calculate the heat of formation of acetic acid if its heat of combustion is –869.0 kJ mol^{–1}. The heat of formation of CO_{2(g)} and H₂O_(l) are –390.0 kJ mol^{–1} and –285.0 kJ mol^{–1} respectively.

SOLUTION :

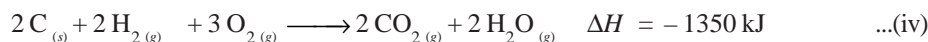
We can frame the following equation from the given data.



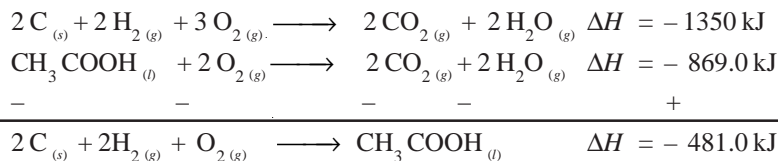
The required equation is



Multiplying equations (iii) and (ii) each by 2 and adding we get

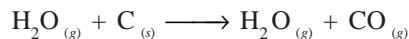


Subtracting (i) from (iv) we have



Thus the heat of formation of acetic acid is **– 481.0 kJ**

SOLVED PROBLEM 15. The standard heats of formation of $\text{CO}_{(g)}$ and $\text{H}_2\text{O}_{(g)}$ at 25°C are 100.5 kJ and -241.8 kJ per mole respectively. Calculate the heat change of following reaction at this temperature.

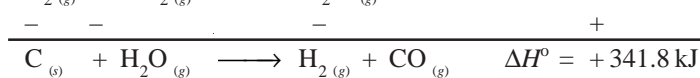
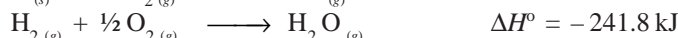
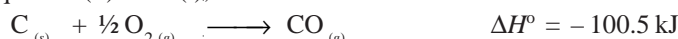


SOLUTION :

We can frame the following equations from the given data

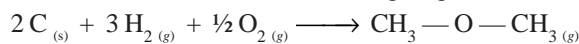


Subtracting equation (ii) from (i), we have



Thus the heat of the reaction is **+342.3 kJ**

SOLVED PROBLEM 16. On the basis of bond energies given below, calculate the heat of reaction :



Bond *Bond energy (kcal mol⁻¹)*

H—H 103

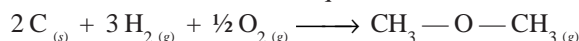
O—O 118

C—H 98

C—O 84

$\text{C}_{(s)} \longrightarrow \text{C}_{(g)}$ 171

SOLUTION : The heat of reaction for the equation



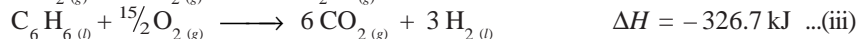
is given by

$$\begin{aligned} \Delta H &= \text{Total bond energy of products} - \text{Total bond energy of reactants} \\ &= [6 \times \text{B.E. of C—H} + 2 \times \text{B.E. of C—O}] - \\ &\quad [2 \times \{\text{C}_{(s)} \longrightarrow \text{C}_{(g)}\} + 3 \times \text{B.E. of H—H} + \frac{1}{2} \times \text{B.E. of O=O}] \\ &= [6 \times 98 + 2 \times 84] - [2 \times 171 + 3 \times 103 + \frac{1}{2} \times 118] \\ &= 756 - 710\text{ kcal} \\ &= \mathbf{46\text{ kcal}} \end{aligned}$$

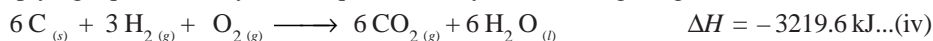
SOLVED PROBLEM 17. The heat of combustion of liquid benzene is -326.7 kJ . The heat of formation of CO_2 and H_2O are -393.5 kJ and -286.2 respectively. Calculate the heat of formation of liquid benzene.

SOLUTION :

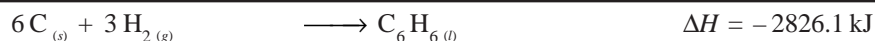
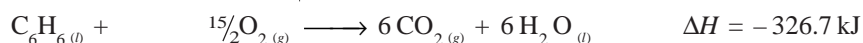
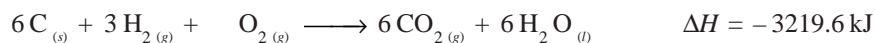
We can frame the following equation from the given data



Multiplying equation (i) by 6 and equation (ii) by 3 and adding we get



Subtracting equation (iii) from equation (iv) we have



Thus the heat of formation of liquid benzene is **-2826.1 kJ**

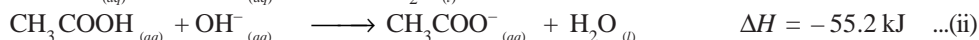
SOLVED PROBLEM 18. The enthalpy of neutralisation of HCl with NaOH is $-57.3 \text{ kJ mol}^{-1}$ and that of CH_3COOH with NaOH is $-55.2 \text{ kJ mol}^{-1}$. Calculate the enthalpy of ionisation of CH_3COOH .

SOLUTION :

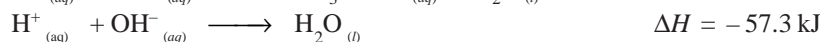
The required equation is



Given that



Subtracting equation (i) from (ii) we have

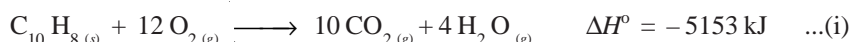


Thus the enthalpy of ionisation of CH_3COOH is **+2.1 kJ**

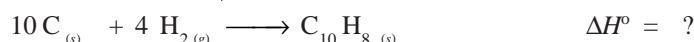
SOLVED PROBLEM 19. Calculate the standard enthalpy of formation of naphthalene (C_{10}H_8) when the standard enthalpy of combustion of naphthalene is -5153 kJ and standard enthalpies of formation of CO_2 and H_2O are $-393.5 \text{ kJ mol}^{-1}$ and $-285.8 \text{ kJ mol}^{-1}$ respectively.

SOLUTION :

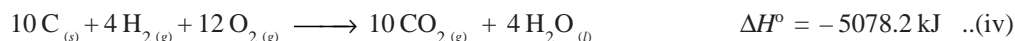
We can frame the following equations from the given data



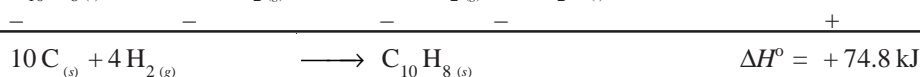
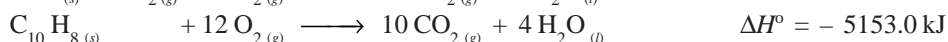
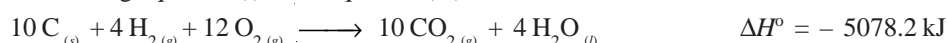
The required equation is



Multiplying equation (ii) by 10 & (iii) by 4 and adding we get



Subtracting equation (i) from equation (iv) we have



Thus standard enthalpy of formation of naphthalene is **+74.8 kJ**

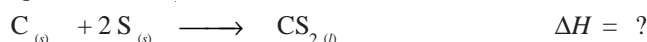
SOLVED PROBLEM 20. Calculate the heat of formation of carbon disulphide. The heat of combustion of CS_2 , S and C are -26.5 kcal , -94.3 kcal and 71.08 kcal respectively at 25°C .

SOLUTION :

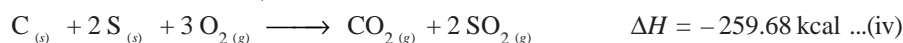
We can frame the following equations from the given data



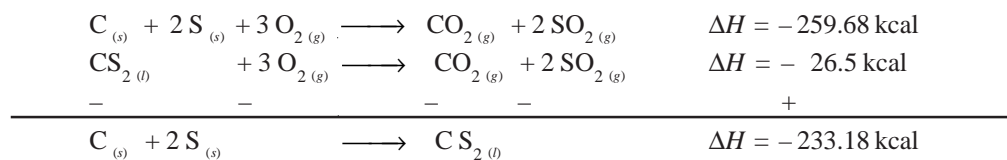
The required equation is



Multiplying equation (ii) by 2 and adding to equation (i) we get



Subtracting equation (iii) from (iv) we have



Thus the heat of formation of CS_2 is -233.18 kcal

SOLVED PROBLEM 21. Using the data (all values are in kcal mol^{-1} at 25°C) given below, calculate the bond energy of $\text{C} - \text{C}$ and $\text{C} - \text{H}$ bonds.

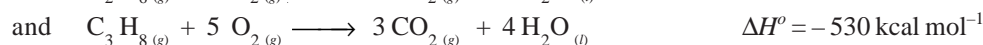
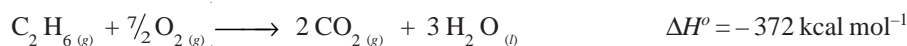
$$\Delta H^\circ_{\text{combustion}}(\text{ethane}) = -372.0 \quad \Delta H^\circ_{\text{combustion}}(\text{propane}) = -530.0$$

$$\Delta H^\circ \text{ for } \text{C}(\text{graphite}) \longrightarrow \text{C}(g) = -172.0 \quad \text{Bond energy of } \text{H} - \text{H} = 104.0$$

$$\Delta H^\circ_f \text{ of } \text{H}_2\text{O}_{(l)} = -68.0 \quad \text{and } \Delta H^\circ_f \text{ of } \text{CO}_2 = -94.0$$

SOLUTION :**(i) To calculate ΔH°_f for ethane and propane**

The chemical equations representing combustion of ethane and propane are



Formula used

$$\Delta H^\circ = \Delta H^\circ_f(\text{Products}) - \Delta H^\circ_f(\text{Reactants})$$

Quantities given (i) For ethane

$$\Delta H^\circ = -372 \text{ kcal mol}^{-1} \quad \Delta H^\circ_f(\text{CO}_2) = -94 \text{ kcal mol}^{-1} \quad \Delta H^\circ_f(\text{H}_2\text{O}) = -68.0 \text{ kcal mol}^{-1}$$

Substitution of values

$$-372 \text{ kcal mol}^{-1} = [2 \times -94 \text{ kcal mol}^{-1} + 3 \times -68 \text{ kcal mol}^{-1}] - [\Delta H^\circ_f(\text{C}_2\text{H}_6) - 0]$$

$$\Delta H^\circ_f(\text{C}_2\text{H}_6) = -392 \text{ kcal mol}^{-1} + 372 \text{ kcal mol}^{-1}$$

$$= 20 \text{ kcal mol}^{-1}$$

Quantities given (ii) For propane

$$\Delta H^\circ = -530 \text{ kcal mol}^{-1} \quad \Delta H^\circ_f(\text{CO}_2) = -94 \text{ kcal mol}^{-1} \quad \Delta H^\circ_f(\text{H}_2\text{O}) = -68.0 \text{ kcal mol}^{-1}$$

Substitution of values

$$-530 \text{ kcal mol}^{-1} = [3 \times -94 \text{ kcal mol}^{-1} + 4 \times -68 \text{ kcal mol}^{-1}] - [\Delta H^\circ_f(\text{C}_3\text{H}_8) - 0]$$

$$\Delta H^\circ_f(\text{C}_3\text{H}_8) = -554 \text{ kcal mol}^{-1} + 530 \text{ kcal mol}^{-1}$$

$$= -24 \text{ kcal mol}^{-1}$$

(ii) To calculate the bond energy of C—C and C—H bonds.

The formation of ethane and propane are represented by



Let the bond energy of C—C be 'a' and that of C—H be 'b'

Formula used

$$\Delta H = \text{Bond energy of reactants} - \text{Bond energy of products}$$

For ethane

$$\begin{aligned} -20 \text{ kcal mol}^{-1} &= [2 \times \text{B.E. of C}_{(graphite)} \longrightarrow \text{C}_{(g)} + 3 \times \text{B.E. of H—H}] - \\ &\quad [1 \times \text{B.E. of C—C} + 6 \times \text{B.E. of C—H}] \\ &= [2 \times 172 + 3 \times 104] - [a + 6b] \\ a + 6b &= 676 \text{ kcal mol}^{-1} \end{aligned}$$

and for propane

$$\begin{aligned} -24 \text{ kcal mol}^{-1} &= [3 \times \text{B.E. of C}_{(graphite)} \longrightarrow \text{C}_{(g)} + 4 \times \text{B.E. of H—H}] - \\ &\quad [2 \times \text{B.E. of C—C} + 8 \times \text{B.E. of C—H}] \\ \text{or } -24 \text{ kcal mol}^{-1} &= [3 \times 172 \text{ kcal mol}^{-1} + 4 \times 104 \text{ kcal mol}^{-1}] - [2a + 8b] \\ \text{or } 2a + 8b &= 956 \text{ kcal mol}^{-1} \end{aligned}$$

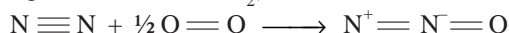
Solving for a and b, we have

$$a = 99 \text{ kcal mol}^{-1} \text{ and } b = 82 \text{ kcal mol}^{-1}$$

SOLVED PROBLEM 22. Calculate the resonance energy of N_2O from the following data : ΔH_f° for $\text{N}_2\text{O} = 82 \text{ kJ mol}^{-1}$. Bond energy of $\text{N}\equiv\text{N}$, $\text{N}=\text{N}$, $\text{O}=\text{O}$ and $\text{N}=\text{O}$ bond are 946, 418, 498, and 607 kJ mol^{-1} respectively.

SOLUTION :

The equation representing the formation of N_2O is

**Formula used**

$$\Delta H_f^\circ(\text{N}_2\text{O}) = \text{B.E. of Reactants} - \text{B.E. of products}$$

Quantities given

$$\text{B.E. of N}\equiv\text{N} = 946 \text{ kJ mol}^{-1}$$

$$\text{B.E. of O}=\text{O} = 498 \text{ kJ mol}^{-1}$$

$$\text{B.E. of N}\equiv\text{N} = 418 \text{ kJ mol}^{-1}$$

$$\text{B.E. of N}=\text{O} = 607 \text{ kJ mol}^{-1}$$

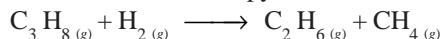
Substitution of values

$$\begin{aligned} \Delta H_f^\circ(\text{N}_2\text{O}) &= [\text{B.E. of N}\equiv\text{N bond} + \frac{1}{2} \text{B.E. of O}=\text{O bond}] - [\text{B.E. of N}=\text{N} + \text{B.E. of N}=\text{O}] \\ &= [946 + \frac{1}{2} \times 498] \text{ kJ mol}^{-1} - [418 + 607] \text{ kJ mol}^{-1} \\ &= 170 \text{ kJ mol}^{-1} \end{aligned}$$

But the actual value of $\Delta H_f^\circ(\text{N}_2\text{O}) = 82 \text{ kJ mol}^{-1}$

$$\begin{aligned} \therefore \text{Resonance energy of N}_2\text{O} &= \text{Theoretical heat of formation} - \text{Actual heat of formation} \\ &= 170 \text{ kJ mol}^{-1} \\ &= 88 \text{ kJ mol}^{-1} \end{aligned}$$

SOLVED PROBLEM 23. Determine the enthalpy of the reaction

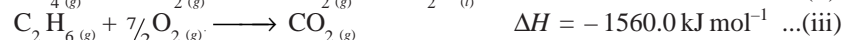
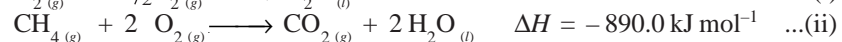


at 25 °C, using the given heats of combustion under standard conditions.

Compound	$\text{H}_{2(g)}$	$\text{CH}_{4(g)}$	$\text{C}_2\text{H}_{6(g)}$	$\text{C}_{(graphite)}$
ΔH° (kJ mol ⁻¹)	-285.8	-890	-1560	-393.5

The standard heat of formation of $\text{C}_3\text{H}_{8(g)}$ is -103.8 kJ mol⁻¹

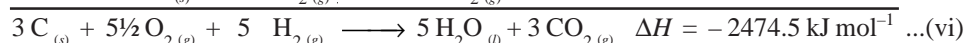
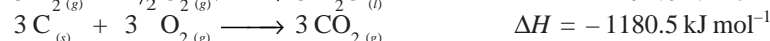
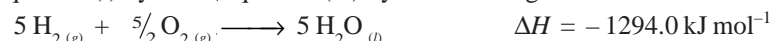
SOLUTION : The given data can be used to frame the following equations



We have to arrive at the equation



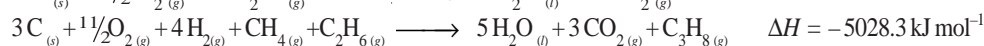
Multiplying equation (i) by 5 and equation (iv) by 3 and adding



Adding equation (ii), (iii) and (v) we get



Subtracting equation (vii) from (vi) we have



SOLVED PROBLEM 24. 0.16 g of methane was subjected to combustion at 27°C in a bomb calorimeter. The temperature of calorimeter system including water was found to rise by 0.5°C. Calculate the heat of combustion of methane at (i) constant volume and (ii) at constant pressure. The thermal capacity of the calorimeter system is 17.7 kJ K⁻¹. ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

SOLUTION :

(i) To calculate the heat of combustion at constant volume

Quantity of heat liberated = Thermal capacity of calorimeter \times Rise in temperature for 0.16 g of methane

$$= 17.7 \text{ kJ K}^{-1} \times 0.5 \text{ K}$$

$$= -8.85 \text{ kJ}$$

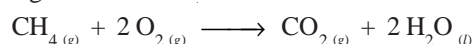
ΔE = Quantity of heat liberated for one mole of methane

$$= \frac{8.85 \text{ kJ} \times 16 \text{ g mol}^{-1}}{0.16 \text{ g}}$$

$$= -885 \text{ kJ}$$

(ii) To calculate the heat of combustion at constant pressure

The equation representing the combustion of methane is



Formula used

$$\Delta H = \Delta E + \Delta n R T$$

Quantities given

$$\Delta E = -885 \text{ kJ mol}^{-1}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$$

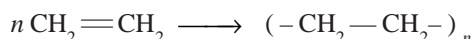
$$T = 27 + 273 = 300 \text{ K}$$

$$\Delta n = n_p - n_R = 1 - 3 = -2$$

Substitution of values

$$\begin{aligned} \Delta H &= -885 \text{ kJ mol}^{-1} + (-2) \times 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol} \times 300 \text{ K} \\ &= -885 - 4.9884 \text{ kJ mol}^{-1} \\ &= \mathbf{-889.9884 \text{ kJ mol}^{-1}} \end{aligned}$$

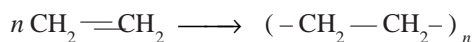
SOLVED PROBLEM 25. The polymerisation of ethylene to linear Polyethylene is represented by the reaction



where n has a large integral value. Given that the average enthalpies of bond dissociation for $\text{C}=\text{C}$ and $\text{C}-\text{C}$ at 298 K are + 590 and + 331 kJ mol^{-1} respectively, calculate the enthalpy of polymerisation per mole of ethylene at 298 K.

SOLUTION :

The polymerisation of ethylene is represented by



For every unit of ethylene $\text{C}=\text{C}$ bond breaks and three new $\text{C}-\text{C}$ single bonds are formed. But the net effect is the formation of two $\text{C}-\text{C}$ single bonds per mole of ethylene *i.e.*

$$\begin{aligned} \text{Total energy released} &= \text{No. of bonds formed} \times \text{Bond energy of } \text{C}-\text{C} \text{ bond} \\ &= 2 \times 331 \text{ kJ mol}^{-1} = 662 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \text{Total energy absorbed} &= \text{No. of bonds broken} \times \text{Bond energy of } \text{C}=\text{C} \text{ bond} \\ &= 1 \times 590 \text{ kJ mol}^{-1} = 590 \text{ kJ mol}^{-1} \end{aligned}$$

$$\therefore \text{Net energy released per mole of ethylene} = 590 \text{ kJ mol}^{-1} - 662 \text{ kJ mol}^{-1}$$

$$\text{Thus } \Delta H \text{ polymeration for ethylene} = \mathbf{-72 \text{ kJ mol}^{-1}}$$

SOLVED PROBLEM 26. At 300K, the enthalpies of formation of Benzoic acid $_{(s)}$, $\text{CO}_2_{(g)}$ and $\text{H}_2\text{O}_{(l)}$ are -408, -393 and -286 kJ mol^{-1} respectively. Calculate the heat of combustion of benzoic acid at (i) constant pressure and (ii) at constant volume. ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

SOLUTION :

(i) To calculate the heat of combustion of $\text{C}_6\text{H}_5\text{COOH}$ at constant pressure.

The equation representing the combustion of benzoic acid is

**Formula used**

$$\Delta H = \Delta H_{f(\text{Products})} - \Delta H_{f(\text{Reactants})}$$

Quantities given

$$\Delta H_f(\text{CO}_2) = -393 \text{ kJ mol}^{-1}$$

$$\Delta H_f(\text{H}_2\text{O}) = -286 \text{ kJ mol}^{-1}$$

$$\Delta H_f(\text{C}_6\text{H}_5\text{COOH}) = -408 \text{ kJ mol}^{-1}$$

Substitution of values

$$\begin{aligned} \Delta H &= [7 \times (-393)] + 3 \times (-286) - [-408 + \frac{15}{2} \times 0] \text{ kJ mol}^{-1} \\ &= [-2751 - 858] + [408] \text{ kJ mol}^{-1} \\ &= \mathbf{-3201 \text{ kJ mol}^{-1}} \end{aligned}$$

(ii) To calculate the heat of combustion at constant volume**Formula used**

$$\Delta H = \Delta E + \Delta n R T$$

Quantities given

$$\Delta H = -320 \text{ kJ mol}^{-1} \quad R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 8.314 \times 10^{-3} \text{ kJ mol}^{-1} \text{ K}^{-1} \quad T = 300 \text{ K}$$

$$\Delta n = n_p - n_R = 7 - \frac{15}{2} = -\frac{1}{2}$$

Substitution of values

$$-320 \text{ kJ mol}^{-1} = \Delta E + (-\frac{1}{2}) \times 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}$$

or

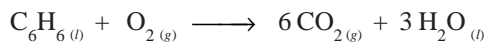
$$\Delta E = -320 \text{ kJ mol}^{-1} + 1.247 \text{ kJ mol}^{-1}$$

$$= \mathbf{318.75 \text{ kJ mol}^{-1}}$$

SOLVED PROBLEM 27. The heat liberated on complete combustion of 7.8 g benzene is 327 kJ. This heat has been measured at constant volume and at 27°C. Calculate the heat of combustion of benzene at constant pressure. ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$)

SOLUTION : (i) To calculate $\Delta H_{(\text{combustion})}$ for benzene per mole

The chemical equation representing combustion of benzene is



Quantity of heat evolved when 7.8 g of benzene is burnt = -327 kJ

Quantity of heat evolved when 78 g (1 mole) of benzene is burnt

$$= - \frac{327 \text{ kJ mol}^{-1} \times 78 \text{ g mol}^{-1}}{7.8 \text{ g}}$$

$$= - 3270 \text{ kJ mol}^{-1}$$

(ii) To calculate ΔE **Formula used**

$$\Delta H = \Delta E + \Delta n R T \quad \text{or} \quad \Delta E = \Delta H - \Delta n R T$$

Quantities given

$$\Delta H = -3270 \text{ kJ mol}^{-1} \quad R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$T = 27 + 273 = 300 \text{ K} \quad \Delta n = n_p - n_R = 6 - \frac{15}{2} = -\frac{3}{2}$$

Substitution of values

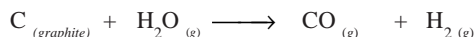
$$\Delta H = -3270 \text{ kJ mol}^{-1} + (-\frac{3}{2}) \times 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}$$

$$= -3270 \text{ kJ mol}^{-1} - 3.741 \text{ kJ mol}^{-1}$$

$$= \mathbf{3273.741 \text{ kJ mol}^{-1}}$$

ADDITIONAL PRACTICE PROBLEMS

1. Calculate the standard internal energy change for the following reaction at 25°C

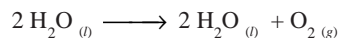


ΔH_f° at 25 °C for $\text{H}_2\text{O}_{(g)} = 241.8 \text{ kJ mol}^{-1}$ and for $\text{CO}_{(g)} = 110.5 \text{ kJ mol}^{-1}$;

Gas constant $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Answer. 128.82 kJ

2. Calculate the standard internal energy change for the following reaction at 25 °C



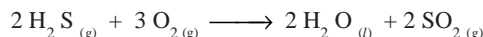
ΔH_f° at 25 °C for $\text{H}_2\text{O}_{(l)}$ = $-188.0 \text{ kJ mol}^{-1}$ and for $\text{H}_2\text{O}_{(l)}$ = $-286.0 \text{ kJ mol}^{-1}$; Gas constant $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Answer. 198.477 kJ

3. The heat of combustion of methane is $-890.65 \text{ kJ mol}^{-1}$ and heats of formation of CO_2 and H_2O are -393.5 and $-286.0 \text{ kJ mol}^{-1}$ respectively. Calculate the heat of formation of methane.

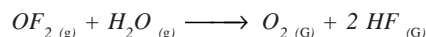
Answer. $-74.85 \text{ kJ mol}^{-1}$

4. Given standard enthalpy of formation of $\text{H}_2\text{O}_{(l)}$, $\text{SO}_{2(g)}$, $\text{H}_2\text{S}_{(g)}$ and $\text{O}_{2(g)}$ are -286 , -296.9 , -20.17 and 0 kJ mol^{-1} respectively. Calculate ΔH_f° for the reaction



Answer. 1125.46 kJ

5. Calculate the standard enthalpy change (ΔH°) and standard internal energy change (ΔE°) for the reaction



when standard enthalpy of formation ΔH_f° for various compounds are $\text{OF}_{2(g)} = -23.0 \text{ kJ mol}^{-1}$,

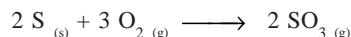
$\text{H}_2\text{O}_{(g)} = -241.8 \text{ kJ mol}^{-1}$ and $\text{HF}_{(g)} = -268.6 \text{ kJ mol}^{-1}$.

Answer. -320.877 kJ

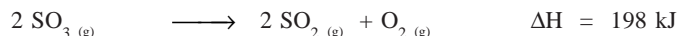
6. Dissociation energy of $\text{H}_{2(g)}$, $\text{Cl}_{2(g)}$ respectively are 435.4 and 243 kJ mol^{-1} . Enthalpy of formation of $\text{HCl}_{(g)}$ is $-92.9 \text{ kJ mol}^{-1}$. Calculate the dissociation energy of HCl .

Answer. $-413.4 \text{ kJ mol}^{-1}$

7. Calculate the enthalpy change for the reaction



given the following information:



Answer. -792 kJ

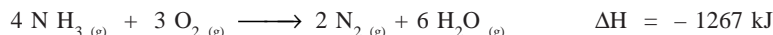
8. While phosphorus, P_4 , burns in an excess of oxygen to form tetraphosphorus decoxide, P_4O_{10} .



what is the heat evolved per gram of phosphorus burnt?

Answer. -23.72 kJ

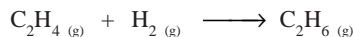
9. Ammonia burns in the presence of a copper catalyst to form nitrogen gas



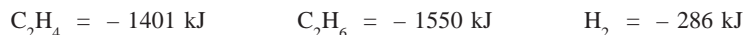
What is the enthalpy change to burn 25.6 ammonia ?

Answer. -476.98 kJ

10. Calculate the enthalpy change for the reaction



using the following combustion data :



Answer. -137 kJ

11. Calcium carbonate on heating decomposes to calcium oxide according to equation



How much heat is required to decompose 24.0 g of calcium carbonate ?

Answer. 42.79 kJ

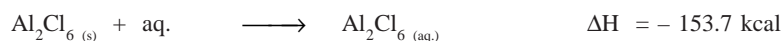
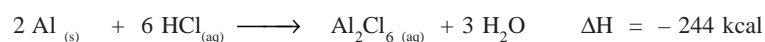
12. In an experiment 5.48 g of formic acid, HCOOH , was burnt and the amount of heat evolved was 30.3 kJ. Calculate ΔH per mole of formic acid.

Answer. 42.79 kJ

13. Calculate the heat of formation of ammonia from the heats of combustion of ammonia and hydrogen which are 9.06 and 68.9 kcals respectively.

Answer. - 94.29 kcals

14. Calculate the heat of formation of anhydrous AlCl_3 from the following data :



Answer. - 327.3 kcals

15. The enthalpies for the following reaction (ΔH°) at 25 °C are given below :



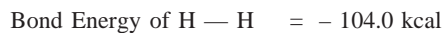
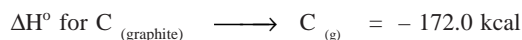
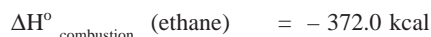
Calculate the O — H bond energy in the hydroxyl radical.

Answer. - 101.19 kcals

16. The bond dissociation energies of gaseous H_2 , Cl_2 and HCl are 104, 58 and 103 kcal mol^{-1} respectively. Calculate the enthalpy of formation of HCl .

Answer. - 22.0 kcal

17. Using the data given below, Calculate the bond of C — C and C — H bonds.

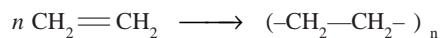


Answer. C — C = 82 kcal ; C — H = 99 kcal

18. In order to get maximum calorific output, a burner should have an optimum fuel to oxygen ratio which corresponds to 3 times as much oxygen as required theoretically for complete combustion of the fuel. A burner which has been adjusted for methane as fuel (with x litre hr^{-1} of CH_4 and 6 x litre hr^{-1} of O_2) is to be readjusted for butane, C_4H_{10} . In order to get the same calorific output what should be the rate of supply of butane and oxygen ? Assume that losses due to incomplete combustion etc. are the same for both fuels and that the gases behave ideally. Heat of combustion : $\text{CH}_4 = 809 \text{ kJ mol}^{-1}$; $\text{C}_4\text{H}_{10} = 2878 \text{ kJ mol}^{-1}$

Answer. butane = 0.2795 x litre hr^{-1} ; $\text{O}_2 = 5.450 \text{ x litre hr}^{-1}$

19. The polymerisation of ethylene to linear polyethylene is represented by the reaction



where n has a large integral value. Given that the average enthalpies of bond dissociation for $\text{C}=\text{C}$ and $\text{C}-\text{C}$ at 298 K are $+590$ and $+331 \text{ kJ mol}^{-1}$ respectively, calculate the enthalpy of polymerisation per mole of ethylene at 298 K.

Answer. -72 kJ mol^{-1}

20. The heat of combustion of $\text{C}_2\text{H}_4(\text{g})$, $\text{C}_2\text{H}_6(\text{g})$ and $\text{H}_2(\text{g})$ are -1409 kJ , -1558.3 kJ and -285.645 respectively. Calculate the heat of hydrogenation of ethylene.

Answer. -136.8 kJ

21. When 2 moles of ethane are completely burnt 3129 kJ of heat is liberated. Calculate the heat of formation, ΔH_f for C_2H_6 . ΔH_f for $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are -395 and -286 kJ respectively.

Answer. -83.5 kJ

22. The standard heat of formation of $\text{CH}_4(\text{g})$, $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ are -76.2 , -394.8 and $-241.6 \text{ kJ mol}^{-1}$ respectively. Calculate the amount of heat evolved by burning 1 m^3 of methane measured under normal condition.

Answer. $3.58 \times 10^4 \text{ kJ}$

9

Second Law of Thermodynamics

CHAPTER

KEY CONCEPTS AND EQUATIONS



ENTROPY, S

It is a measure of the disorder or freedom or randomness of a system. The increasing order of entropy is

$$\text{Solid} < \text{Liquid} < \text{Gas}$$

It is denoted by S . It is a thermodynamics quantity depending upon the initial and final states of the system. It is independent of path. The change in entropy, ΔS , is given by

$$\Delta S = S_f - S_i$$

where S_f is the final entropy and S_i the initial entropy. The change in entropy for a reaction is given by

$$\Delta S = \sum S_{(\text{Products})} - \sum S_{(\text{Reactants})}$$

ΔS will be +ve if the system is more disorganised in the final state (products) and it will be -ve if the system is less disorganised in the final state. The units of entropy are JK^{-1} or cal K^{-1}

SECOND LAW OF THERMODYNAMICS

The total entropy of the universe is increasing *i.e.* the total entropy of a system and its surrounding is always increasing, *i.e.*

$$\Delta S > \frac{q}{T}$$

Thus for a spontaneous process at a given temperature the change in entropy of the system is greater than the heat divided by the absolute temperature.

EFFICIENCY OF A HEAT ENGINE, η

It is the ratio of work obtained in cyclic process (w) to the heat taken from the high temperature reservoir *i.e.*

$$\eta = \frac{w}{q_2} = \frac{T_2 - T_1}{T_2}$$

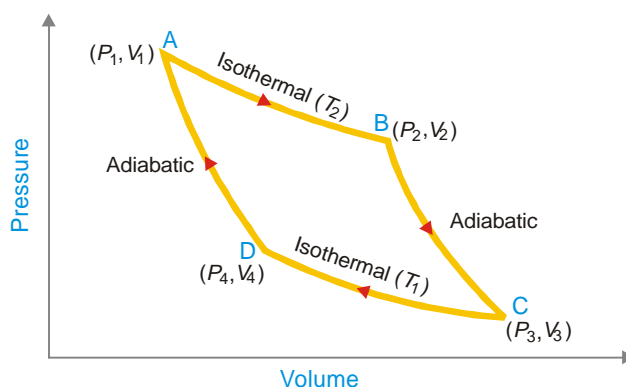
where T_2 and T_1 are the absolute temperatures of the reservoir and sink respectively.

THE CARNOT CYCLE

The cycle of processes which occurred under reversible conditions is referred to as the Carnot cycle. It comprises of four operations :

- (i) Isothermal reversible expansion (ii) Adiabatic reversible expansion
- (iii) Isothermal reversible compression (iv) Adiabatic reversible compression

These four operations are shown in the Fig 9.1.



■ **Figure 9.1**
The Carnot cycle.

Work done and heat absorbed in Carnot cycle. The work done in Carnot cycle is given by

$$w = R T_2 \ln \frac{V_2}{V_1} + R T_1 \ln \frac{V_4}{V_3}$$

and the heat absorbed in Carnot cycle is given by

$$q = R T_2 \ln \frac{V_2}{V_1} - R T_1 \ln \frac{V_3}{V_4}$$

or

$$q = R (T_2 - T_1) \ln \frac{V_2}{V_1} \quad \left[\because \frac{V_3}{V_4} = \frac{V_2}{V_1} \right]$$

More statements of Second Law of Thermodynamics

- (1) It is impossible to take heat from a hotter reservoir and convert it completely into work by a cyclic process without transferring a part of heat to a cooler reservoir.
- (2) It is possible for a cyclic process to transfer heat from a body at lower temperature to one at higher temperature without at the same time converting some heat to work.

THIRD LAW OF THERMODYNAMICS

All substances in their normal crystalline state at absolute zero would be the most ordered state with zero entropy. This is third law of Thermodynamics.

Entropy change for an ideal gas

It is given by

$$\Delta S = 2.303 n C_v \log \frac{T_2}{T_1} + 2.303 R \log \frac{V_2}{V_1}$$

or

$$\Delta S = 2.303 n C_p \log \frac{T_2}{T_1} + 2.303 n R \log \frac{P_1}{P_2}$$

Special Cases

Case I : At constant temperature for an isothermal process

$$\Delta S_T = 2.303 n R \log \frac{P_1}{P_2}$$

Case II : At constant pressure (Isobaric process)

$$\Delta S_p = 2.303 n C_p \log \frac{T_2}{T_1}$$

Case III : At constant volume (Isochoric process)

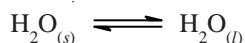
$$\Delta S_v = 2.303 n C_v \log \frac{T_2}{T_1}$$

Entropy change accompanying change of phase

Certain processes occur at equilibrium, *e.g.* melting of ice at 273 K when ice is in equilibrium with liquid water. In such cases the entropy change results from the absorption of heat energy. Thus

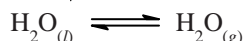
$$\Delta S = \frac{\Delta H}{T}$$

For example



$$\Delta S_{\text{fusion}} = \frac{\Delta H_{\text{fusion}}}{T_m}$$

and



$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_b}$$

where T_m and T_b are the absolute temperature at which melting and boiling of water occur.

GIBBS FREE ENERGY

The work accompanying a chemical process may be of two types - unavoidable (work of expansion) and useful work (work of non - expansion). Therefore, every system has a capacity to do useful work which is called Gibbs Free Energy, G , defined by the relation.

$$G = H - TS$$

and the change in free energy, ΔG , is given by

$$\Delta G = \Delta H - T\Delta S$$

under standard conditions (298 K and 1 atm pressure) we have

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

when all reactants and products are in their standard states.

GIBBS HELMHOLTZ EQUATION

(i) In terms of free energy and enthalpy

$$\Delta G = \Delta H - T d \left(\frac{\Delta G}{dT} \right)_p$$

(ii) In terms of Internal energy and work function

$$\Delta A = \Delta E + T d \left(\frac{\Delta A}{dT} \right)_v$$

SPONTANEOUS REACTIONS AND CRITERION FOR SPONTANEITY

A reaction is spontaneous if the capacity of the system to do work increases during the process. In term of ΔG

the process is spontaneous if $\Delta G = -ve$

and the process is non - spontaneous if $\Delta G = +ve$

Since ΔG is the net resultant of two factors ΔH and $T\Delta S$, it becomes negative under the conditions given in Table 10.1.

TABLE 10.1. CONDITIONS FOR SPONTANEITY OF A REACTION			
ΔH	ΔS	ΔG	Spontaneity
-ve	+ve	-ve	Spontaneous at all temperatures.
+ve	-ve	+ve	Non-spontaneous at all temperatures.
-ve	-ve	$\begin{cases} +ve \\ \text{or} \\ -ve \end{cases}$	Non-spontaneous at high temperatures. Spontaneous at low temperatures.
+ve	+ve	$\begin{cases} +ve \\ \text{or} \\ -ve \end{cases}$	Non-spontaneous at low temperatures. Spontaneous at high temperatures.

CLAUSIUS CLAPEYRON EQUATION

It gives us important information about a system of any two phases of a single substance in chemical equilibrium. It is given by

$$\log \frac{p_2}{p_1} = \frac{\Delta H}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

where p_2 is the vapour pressure at temperature T_1 , p_1 the vapour pressure at temperature T_2 , ΔH is the heat of reaction and R is gas constant.

VAN'T HOFF ISOTHERM AND ISOCHORE

The equilibrium constant is related to the Gibbs free energy by the relation

$$-\Delta G = R T \ln K_p$$

or

$$-\Delta G = 2.303 R T \log K_p$$

And the variation of equilibrium constant with temperature is given by

$$\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H}{2.303 \times R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. What is the change in entropy when 1 mole of helium gas is heated from 200K to 400K at constant pressure ? (Given: C_p for helium = 5.0 cal per degree per mole)

SOLUTION :

Formula used

$$\Delta S = 2.303 n C_p \log \frac{T_2}{T_1}$$

Quantities given

$$n = 1 \text{ mole}$$

$$C_p = 5.0 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$T_1 = 200\text{K}$$

$$T_2 = 400 \text{ K}$$

Substitution of values

$$\begin{aligned} \Delta S &= 2.303 \times 1 \text{ mole} \times 5 \text{ cal K}^{-1} \text{ mol}^{-1} \times \log \frac{400\text{K}}{200\text{K}} \\ &= 11.515 \text{ cal K}^{-1} \times \log 2 \\ &= 11.515 \times 0.3010 \text{ cal K}^{-1} \\ &= \mathbf{3.466 \text{ cal K}^{-1}} \end{aligned}$$

SOLVED PROBLEM 2. Calculate the total entropy change when 5 gram of ice at 0 °C is converted into steam at 100 °C. (Latent heat of evaporation = 540 cal/g ; C_p for water = 18 cal/mole ; Latent heat of fusion of water = 80 cal/mole).

SOLUTION :

(i) To calculate the entropy change for 5g of ice at 0 °C to water at 0 °C.

Formula used

$$\Delta S_f = \frac{\Delta H_f}{T_f}$$

Quantities given

$$\Delta H_f = 5 \times 80 \text{ cal}$$

$$T_f = 273 \text{ K}$$

Substitution of values

$$\begin{aligned} \Delta S_f &= \frac{5 \times 80 \text{ cal}}{273 \text{ K}} \\ &= 1.465 \text{ cal K}^{-1} \end{aligned}$$

(ii) To calculate the entropy change for 5g water at 0 °C to water at 100 °C**Formula used**

$$\Delta S_2 = 2.303 C_p \log \frac{T_2}{T_1}$$

Quantities given

$$\begin{aligned} T_1 &= 273 \text{ K} & T_2 &= 373 \text{ K} \\ C_p &= 18 \text{ cal mol}^{-1} & \text{or } C_p \text{ for 5g} &= 5 \text{ cal} \end{aligned} \quad [\because 1 \text{ mole} = 18 \text{g}]$$

Substitution of values

$$\begin{aligned} \Delta S &= 2.303 \times 5 \text{ cal} \times \log \frac{373 \text{ K}}{273 \text{ K}} \\ &= 11.515 \text{ cal} \times 0.1355 \\ &= 1.560 \text{ cal K}^{-1} \end{aligned}$$

(iii) Entropy change for 5g of water at 100 °C to steam at 100 °C.**Formula used**

$$\Delta S_3 = \frac{\Delta H_v}{T_b}$$

Quantities given

$$\Delta H_v = 540 \text{ cal g}^{-1} \times 5 \text{ g} = 2700 \text{ cal} \quad T_b = 373 \text{ K}$$

Substitution of values

$$\begin{aligned} \Delta S_3 &= \frac{2700 \text{ cal}}{373 \text{ K}} \\ &= 7.238 \text{ cal K}^{-1} \end{aligned}$$

Total entropy change

$$\begin{aligned} \Delta S &= \Delta S_1 + \Delta S_2 + \Delta S_3 \\ &= 1.465 \text{ cal K}^{-1} + 1.560 \text{ cal K}^{-1} + 7.238 \text{ cal K}^{-1} \\ &= \mathbf{10.263 \text{ cal K}^{-1}} \end{aligned}$$

SOLVED PROBLEM 3. Calculate the work performed when two grams of hydrogen gas is expanded isothermally and reversibly at 27 °C from ten to one hundred litres. What is the amount of heat absorbed ? What is the change in internal energy ?

SOLUTION :**(i) To calculate the work done in an isothermal reversible expansion****Formula used**

$$w = n R T \times 2.303 \log \frac{V_2}{V_1}$$

Quantities given

$$\begin{aligned} n &= \frac{2 \text{ g}}{2 \text{ g mol}^{-1}} = 1 \text{ mole} & V_1 &= 10 \text{ litres} & V_2 &= 100 \text{ litres} \\ T &= 300 \text{ K} & R &= 1.987 \text{ cal K}^{-1} \text{ mol}^{-1} \end{aligned}$$

Substitution of values

$$\begin{aligned} w &= 2.303 \times 1 \text{ mole} \times 1.987 \text{ cal K}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \times \log \frac{100 \text{ lit}}{10 \text{ lit}} \\ &= \mathbf{1372.82 \text{ cal}} \end{aligned}$$

(ii) To calculate the heat absorbed in the process

For this process

$$q = w = \mathbf{1372.82 \text{ cal}}$$

and

$$\Delta E = q - w$$

$$= 1372.82 \text{ cal} - 1372.82 \text{ cal}$$

$$= 0$$

SOLVED PROBLEM 4. For a heat engine the source is at 500 K and the sink at 300 K. What is the efficiency of this engine ?

SOLUTION :

Formula used

$$\eta = \frac{T_2 - T_1}{T_2}$$

Quantities given

$$T_2 = 500 \text{ K}$$

$$T_1 = 300 \text{ K}$$

Substitution of values

$$\begin{aligned} \text{Efficiency, } \eta &= \frac{500 \text{ K} - 300 \text{ K}}{500 \text{ K}} \\ &= \frac{200}{500} \\ &= \mathbf{0.4 \text{ or } 40\%} \end{aligned}$$

SOLVED PROBLEM 5. Calculate the work done in the expansion of 3 moles of hydrogen reversibly and isothermally at 27 °C from 21.0 litres to 70.3 litres.

SOLUTION :

Formula used

$$w = 2.303 \times n R T \log \frac{V_2}{V_1}$$

Quantities given

$$n = 3 \text{ moles}$$

$$R = 8.314 \times 10^7 \text{ ergs}$$

$$T = 300 \text{ K}$$

$$V_1 = 21 \text{ litres}$$

$$V_2 = 70.3 \text{ litres}$$

Substitution of values

$$\begin{aligned} w &= 2.303 \times 3 \text{ moles} \times 8.314 \times 10^7 \text{ ergs} \times 300 \text{ K} \times \log \frac{70.3 \text{ lit}}{21 \text{ lit}} \\ &= 17232.43 \times 10^7 \text{ erg} \times \log \frac{70.3}{21} \\ &= 17232.43 \times 10^7 \text{ erg} \times \log 3.3490 \\ &= 17232.43 \times 10^7 \text{ erg} \times 0.5249 \\ &= \mathbf{9045.30 \times 10^7 \text{ ergs}} \end{aligned}$$

SOLVED PROBLEM 6. Heat supplied to a Carnot engine is 1897.86 kJ. How much useful work can be done by the engine which works between 0 °C and 100 °C ?

SOLUTION :

Formula used

$$\frac{w}{q_2} = \frac{T_2 - T_1}{T_2}$$

or

$$w = q_2 \times \frac{T_2 - T_1}{T_2}$$

Quantities given

$$q_2 = 1897.86 \text{ kJ}$$

$$T_2 = 100 + 273 = 373 \text{ K}$$

$$T_1 = 0 + 273 = 273 \text{ K}$$

Substitution of values

$$w = 1897.86 \text{ kJ} \times \frac{373 \text{ K} - 273 \text{ K}}{373 \text{ K}}$$

$$\begin{aligned}
 &= 1897.86 \text{ kJ} \times \frac{100}{373} \\
 &= \mathbf{508.81 \text{ kJ}}
 \end{aligned}$$

SOLVED PROBLEM 7. A Carnot's engine works between the temperatures 27°C and 127°C . Calculate the efficiency of the engine.

SOLUTION :

Formula used :

$$\text{Efficiency, } \eta = \frac{T_2 - T_1}{T_2}$$

Quantities given

$$T_1 = 27 + 273 = 300 \text{ K}$$

$$T_2 = 127 + 273 = 400 \text{ K}$$

Substitution of values

$$\begin{aligned}
 \text{Efficiency, } \eta &= \frac{400 \text{ K} - 300 \text{ K}}{400 \text{ K}} \\
 &= \frac{100}{400} \\
 &= \mathbf{0.25 \text{ or } 25\%}
 \end{aligned}$$

SOLVED PROBLEM 8. Calculate the work done on the system if one mole of an ideal gas at 300 K is compressed isothermally and reversibly to one-fifth of its original volume.

SOLUTION :

Formula used

$$w = 2.303 \times n R T \log \frac{V_2}{V_1}$$

Quantities given

$$n = 1 \text{ mole}$$

$$R = 8.314 \times 10^7 \text{ ergs}$$

$$T = 300 \text{ K}$$

$$V_1 = V \text{ litres}$$

$$V_2 = \frac{V}{5} \text{ litres}$$

Substitution of values

$$\begin{aligned}
 w &= 2.303 \times 1 \text{ mole} \times 8.314 \times 10^7 \text{ ergs} \times 300 \text{ K} \times \log \frac{V}{5 \times V} \\
 &= 5744.14 \times 10^7 \text{ ergs} \times \log \frac{1}{5} \\
 &= 5744.14 \times 10^7 \text{ ergs} \times (-0.6990) \\
 &= \mathbf{-4015.15 \times 10^7 \text{ ergs}}
 \end{aligned}$$

SOLVED PROBLEM 10. Two moles of an ideal gas undergo isothermal reversible expansion from 15 litres to 30 litres at 300 K. Calculate the work done and change in entropy.

SOLUTION :

(i) To calculate the work done

Formula used

$$w = 2.303 \times n R T \log \frac{V_2}{V_1}$$

Quantities given

$$n_2 = 2 \text{ moles}$$

$$R = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$T = 300 \text{ K}$$

$$V_1 = 15 \text{ litres}$$

$$V_2 = 30 \text{ litres}$$

Substitution of values

$$w = 2.303 \times 2 \text{ mole} \times 1.987 \text{ cal K}^{-1} \text{ mol}^{-1} \times 300 \times \log \frac{30 \text{ lit}}{15 \text{ lit}}$$

$$\begin{aligned}
 &= 2745.637 \text{ cal} \times \log 2 \\
 &= 2745.637 \text{ cal} \times 0.3010 \\
 &= \mathbf{826.4 \text{ cal}}
 \end{aligned}$$

(ii) To calculate the change in entropy**Formula used**

$$\Delta S = \frac{q}{T}$$

Quantities given

$$q = 826.4 \text{ cal}$$

$$T = 300 \text{ K}$$

Substitution of values

$$\begin{aligned}
 \Delta S &= \frac{826.4 \text{ cal}}{300 \text{ K}} \\
 &= \mathbf{2.755 \text{ cal K}^{-1}}
 \end{aligned}$$

SOLVED PROBLEM 11. Water boils at 373 K at one atm pressure. At what temperature will it boil at a hill station where the atmospheric pressure is 500 mm. Hg. (Latent heat of vaporisation of water is 2.3 kJg^{-1} and $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$).

SOLUTION :**Formula used**

$$\log \frac{p_2}{p_1} = \frac{\Delta H}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

Quantities given

$$p_2 = 500 \text{ mm}$$

$$p_1 = 760 \text{ mm}$$

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\text{Latent heat of vaporisation of water} = 2.3 \text{ kJg}^{-1} = 2300 \text{ J g}^{-1}$$

$$T_1 = 373 \text{ K}$$

Substitution of values

$$\log \frac{500 \text{ mm}}{760 \text{ mm}} = \frac{2300 \text{ Jg}^{-1} \times 18 \text{ g mol}^{-1}}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1}} \left[\frac{1}{373} - \frac{1}{T_2} \right]$$

$$-0.1818 = 2162.2025 \left[\frac{1}{373} - \frac{1}{T_2} \right]$$

$$-0.1818 = \frac{2162.2025}{373} - \frac{2162.2025}{T_2} \text{ K}$$

$$\text{or} \quad \frac{2162.2025}{T_2} = 5.796 + 0.1818$$

$$= 5.9785 \text{ K}$$

$$\text{or} \quad T_2 = \frac{2162.2025}{5.9785} \text{ K}$$

$$= \mathbf{361.65 \text{ K}}$$

SOLVED PROBLEM 12. Calculate the work performed when 4 moles of an ideal gas expand isothermally and reversibly at 25°C from 15 to 20 dm^3 . ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$).

SOLUTION :**Formula used**

$$w = 2.303 \times n R T \log \frac{V_2}{V_1}$$

Quantities given

$$n = 4 \text{ moles}$$

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$T = 25 + 273 = 298 \text{ K}$$

$$V_1 = 15 \text{ dm}^3$$

$$V_2 = 20 \text{ dm}^3$$

Substitution of values

$$\begin{aligned} w &= 2.303 \times 4 \text{ mole} \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \log \frac{20 \text{ dm}^3}{15 \text{ dm}^3} \\ &= 22823.39 \text{ J} \times \log \frac{4}{3} \\ &= 22823.39 \text{ J} \times 0.1250 \\ &= 2852.92 \text{ J} \\ &= \mathbf{2.85292 \text{ kJ}} \end{aligned}$$

SOLVED PROBLEM 13. An engine operates between 100°C and 0°C and another engine operates between 100°C and 0 K (absolute zero). Find the efficiency in two cases.

SOLUTION :**(i) For engine A operating between 100°C and 0°C** **Formula used**

$$\eta = \frac{T_2 - T_1}{T_2}$$

Quantities given

$$T_2 = 100 + 273 = 373 \text{ K}$$

$$T_1 = 0 + 273 = 273 \text{ K}$$

Substitutions of values

$$\begin{aligned} \eta &= \frac{373 \text{ K} - 273 \text{ K}}{373 \text{ K}} \\ &= \frac{100}{373} \\ &= 0.268 \text{ or } 26.8\% \end{aligned}$$

(ii) For engine B operating between 100°C and 0 K **Formula used**

$$\eta = \frac{T_2 - T_1}{T_2}$$

Quantities given

$$T_2 = 100 + 273 = 373 \text{ K}$$

$$T_1 = 0 \text{ K}$$

Substitution of values

$$\begin{aligned} \eta &= \frac{373 \text{ K} - 0 \text{ K}}{373 \text{ K}} \\ &= \frac{373}{373} \\ &= 1 \text{ or } 100\% \end{aligned}$$

SOLVED PROBLEM 14. Two moles of hydrogen are compressed adiabatically from NTP conditions to occupy a volume of 4.48 litre. Calculate the final pressure and temperature. ($\gamma = 1.41$)

SOLUTION :

(i) To calculate the final pressure

Formula used

$$P_1 V_1^\gamma = P_2 V_2^\gamma \quad \text{or} \quad \frac{P_1}{P_2} = \left(\frac{V_2}{V_1} \right)^\gamma$$

Quantities given

$$P_1 = 1 \text{ atm}$$

$$T_1 = 273 \text{ K}$$

$$\gamma = 1.41$$

$$V_1 = 44.8 \text{ litre}$$

$$V_2 = 4.48 \text{ litre}$$

Substitution of values

$$\frac{1 \text{ atm}}{P_2} = \left(\frac{4.48 \text{ litre}}{44.8 \text{ litre}} \right)^{1.41 \text{ atm}}$$

$$\frac{1}{P_2} = \left(\frac{1}{10} \right)^{1.41 \text{ atm}}$$

or

$$P_2 = 10^{1.41}$$

Taking logarithms

$$\log P_2 = 1.41 \times \log 10$$

$$\log P_2 = 1.41 \text{ atm} \quad [\because \log 10 = 1]$$

or

$$\begin{aligned} P_2 &= \text{Antilog } 1.41 \text{ atm} \\ &= \mathbf{25.7 \text{ atm}} \end{aligned}$$

(ii) To calculate the final temperature

Formula used

$$P_2 V_2 = n R T_2 \quad \text{or} \quad T_2 = \frac{P_2 V_2}{n R}$$

Quantities given

$$n = 2 \text{ moles}$$

$$R = 0.0820 \text{ atm lit K}^{-1} \text{ mol}^{-1}$$

$$P_2 = 25.7 \text{ atm}$$

$$V_2 = 4.48 \text{ litre}$$

Substitution of values

$$\begin{aligned} T_2 &= \frac{25.7 \text{ atm} \times 4.48 \text{ lit}}{0.0820 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 2 \text{ mol}} \\ &= 702.1 \text{ K} \\ &= 702.1 - 273 \\ &= \mathbf{429.1^\circ \text{C}} \end{aligned}$$

SOLVED PROBLEM 15. Calculate the change in free energy for the expansion of one mole of an ideal gas from 2.0 atm to 0.2 atm at 25 °C ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$).

SOLUTION :

Formula used

$$\Delta G = 2.303 \times n R T \log \frac{P_2}{P_1}$$

Quantities given

$$n = 1 \text{ mole}$$

$$T = 298 \text{ K}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$P_1 = 2 \text{ atm}$$

$$P_2 = 0.2 \text{ atm}$$

Substitution of values

$$\begin{aligned} \Delta G &= 2.303 \times 1 \text{ mole} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \log \frac{0.2 \text{ atm}}{2.0 \text{ atm}} \\ \Delta G &= 5705.848 \text{ J} \times \log \frac{1}{10} \\ &= 5705.8483 \text{ J} \times (-1.0) \\ &= -5705.8483 \text{ J} \end{aligned}$$

SOLVED PROBLEM 16. For the reaction $\text{H}_{2(g)} + \frac{1}{2} \text{O}_{2(g)} \longrightarrow \text{H}_2\text{O}_{(l)}$ the values of enthalpy change and free energy change are -68.32 and -56.69 kcal respectively at 25 °C. Calculate the value of free energy change at 30 °C.

SOLUTION :

(i) To calculate

Formula used

$$\left[\frac{\delta(\Delta G)}{\delta T} \right]_P$$

$$\Delta G = \Delta H + T \left[\frac{\delta(\Delta G)}{\delta T} \right]_P$$

Quantities given

$$\Delta G = -56.69 \text{ kcal}$$

$$\Delta H = -68.32 \text{ kcal}$$

$$T = 25 + 273 = 298 \text{ K}$$

Substitution of values

$$\begin{aligned} -56.69 \text{ kcal} &= -68.32 \text{ kcal} + 298 \text{ K} \left[\frac{\delta(\Delta G)}{\delta T} \right]_P \\ \text{or} \quad \left[\frac{\delta(\Delta G)}{\delta T} \right]_P &= \frac{-56.69 \text{ kcal} + 68.32 \text{ kcal}}{298 \text{ K}} \\ &= \frac{11.630 \text{ kcal}}{298 \text{ K}} \\ &= 0.0390 \text{ kcal K}^{-1} \end{aligned}$$

(ii) To calculate ΔG at 30 °C

Assuming that $\left[\frac{\delta(\Delta G)}{\delta T} \right]_P$ remains constant over this temperature range.

Formula used

$$\Delta G = \Delta H + T \left[\frac{\delta(\Delta G)}{\delta T} \right]_P$$

Quantities given

$$\Delta H = -68.32 \text{ kcal}$$

$$T = 30 + 273 = 303 \text{ K} \quad \left[\frac{\delta(\Delta G)}{\delta T} \right]_P = 0.0390 \text{ kcal K}^{-1}$$

Substitution of values

$$\Delta G = -68.32 \text{ kcal} + 303 \text{ K} \times 0.0390 \text{ kcal K}^{-1}$$

$$\begin{aligned}
 &= -68.32 \text{ kcal} + 11.817 \text{ kcal} \\
 &= -57.15 \text{ kcal.}
 \end{aligned}$$

SOLVED PROBLEM 17. 1.0 mole of steam is condensed at 100°C and water is cooled to 0 °C and frozen to ice. Calculate the entropy change for the process. Latent heat of fusion and evaporation of ice and water are 80 and 540 cal/g respectively.

SOLUTION :

(i) To calculate the entropy change for 1 mole of steam of 100 °C to water at 100 °C

Formula used

$$\Delta S_1 = \frac{\Delta H_v}{T_b}$$

Quantities given

$$\Delta H_v = 540 \text{ cal g}^{-1} \times 18 \text{ g} \quad T_b = 373 \text{ K}$$

Substitution of values

$$\Delta S_1 = \frac{540 \text{ cal g}^{-1} \times 18 \text{ g mol}^{-1}}{373 \text{ K}} = 26.06 \text{ cal K}^{-1} \text{ mol}^{-1}$$

(ii) To calculate entropy change for 1 mole of water at 100 °C to water at 0 °C

Formula used

$$\Delta S_2 = C_p \times 2.303 \times \log \frac{T_2}{T_1}$$

Quantities given

$$T_1 = 373 \text{ K} \quad T_2 = 273 \text{ K} \quad C_p = 18 \text{ cal K}^{-1} \text{ mol}^{-1}$$

Substitution of values

$$\begin{aligned}
 \Delta S_2 &= 18 \text{ cal K}^{-1} \text{ mol}^{-1} \times 2.303 \times \log \frac{273 \text{ K}}{373 \text{ K}} \\
 &= 41.45 \text{ cal K}^{-1} \text{ mol}^{-1} \times (-0.1355) \\
 &= -5.617 \text{ cal K}^{-1} \text{ mol}^{-1}
 \end{aligned}$$

(iii) To calculate entropy change for 1 mole of water at 0 °C to ice at 0 °C

Formula used

$$\Delta S_3 = \frac{\Delta H_f}{T_f}$$

Quantities given

$$\Delta H_f = 80 \text{ cal g}^{-1} \times 18 \text{ g mol}^{-1} \quad T_f = 273 \text{ K}$$

Substitution of values

$$\begin{aligned}
 \Delta S_3 &= \frac{80 \text{ cal g}^{-1} \times 18 \text{ g mol}^{-1}}{273 \text{ K}} \\
 &= 5.275 \text{ cal K}^{-1} \text{ mol}^{-1}
 \end{aligned}$$

Total entropy change

$$\begin{aligned}
 \Delta S &= \Delta S_1 + \Delta S_2 + \Delta S_3 \\
 \Delta S &= 26.06 \text{ cal K}^{-1} \text{ mol}^{-1} + (-5.618 \text{ cal K}^{-1} \text{ mol}^{-1}) + 5.274 \text{ cal K}^{-1} \text{ mol}^{-1} \\
 &= 25.717 \text{ cal K}^{-1} \text{ mol}^{-1}
 \end{aligned}$$

SOLVED PROBLEM 18. 5.0 moles of an ideal gas ($C_v = 5/2 R$) are allowed to expand adiabatically and reversibly at 300 K from a pressure of 10 atm to 1 atm. Calculate the final temperature and work done by the gas.

SOLUTION :**(i) To calculate the final temperature****Formula used**

$$\frac{T_2}{T_1} = \left(\frac{P_1}{P_2} \right)^{\frac{1-\gamma}{\gamma}}$$

Quantities given

$$T_1 = 300 \text{ K}$$

$$P_1 = 10 \text{ atm}$$

$$P_2 = 1 \text{ atm}$$

$$\gamma = 1.4$$

Substitution of values

$$\frac{T_2}{300 \text{ K}} = \left(\frac{10}{1} \right)^{\frac{1-1.4}{1.4}}$$

or

$$T_2 = 300 \text{ K} \times 10^{-\frac{0.4}{1.4}}$$

Taking logarithms

$$\begin{aligned} \log T_2 &= \log 300 + \left(\frac{-0.4}{1.4} \right) \log 10 \\ &= 2.4771 - 0.2857 \\ &= 2.1914 \end{aligned}$$

Taking antilogarithms

$$\begin{aligned} T_2 &= \text{Antilog } 2.1914 \\ &= \mathbf{155.38 \text{ K}} \end{aligned}$$

(ii) To calculate the work done in an adiabatic process**Formula used**

$$\begin{aligned} w &= C_v (T_2 - T_1) \\ &= \frac{5}{2} R \times (T_2 - T_1) \end{aligned}$$

Quantities given

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$T_2 = 155.38 \text{ K}$$

$$T_1 = 300 \text{ K}$$

Substitution of values

$$\begin{aligned} w &= \frac{5}{2} \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times (155.38 - 300) \text{ K} \\ &= \mathbf{-3005.93 \text{ J}} \end{aligned}$$

SOLVED PROBLEM 19. Calculate the entropy increase in the evaporation of a mole of water at 100 °C. (Heat of vaporisation = 540 cal g⁻¹)

SOLUTION :**Formula used**

$$\Delta S_v = \frac{\Delta H_v}{T_b}$$

Quantities given

$$\Delta H_v = 540 \text{ cal g}^{-1} = 540 \text{ cal g}^{-1} \times 18 \text{ g mol}^{-1}$$

$$T_b = 100 + 273 = 373 \text{ K}$$

Substitution of values

$$\begin{aligned} \Delta H_v &= \frac{540 \times 18 \text{ cal mol}^{-1}}{373 \text{ K}} \\ &= \mathbf{26.06 \text{ cal K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

SOLVED PROBLEM 20. Calculate ΔS when 28 gm of N_2 gas expand reversibly from 2 litres to 20 litres at 27 °C.

SOLUTION :

Formula used

$$\Delta S = 2.303 \times n R \log \frac{V_2}{V_1}$$

Quantities given

$$n = \frac{28 \text{ g}}{14 \text{ g mol}^{-1}} = 2 \text{ moles}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$V_1 = 2 \text{ litres}$$

$$V_2 = 20 \text{ litre}$$

Substitution of values

$$\begin{aligned} \Delta S &= 2.303 \times 2 \text{ mole} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \log \frac{20 \text{ lit}}{2 \text{ lit}} \\ &= 38.294 \text{ J K}^{-1} \times \log 10 \\ &= \mathbf{38.294 \text{ J K}^{-1}} \quad [\because \log 10 = 1] \end{aligned}$$

SOLVED PROBLEM 21. Calculate the entropy change in transforming 24 g of Ice into water at 0 °C. Molar heat of fusion = 6009 J mol⁻¹.

SOLUTION :

Formula used

$$\Delta S_f = \frac{\Delta H_f}{T_f}$$

Quantities given

$$\Delta H_f = 6009 \text{ J mol}^{-1} \quad T_f = 273 \text{ K}$$

$$\Delta H_f \text{ for 24 g of water} = \frac{24}{18} \times 6009 \text{ J} = 8012 \text{ J}$$

Substitution of values

$$\Delta S_f = \frac{8012 \text{ J}}{273 \text{ K}} = \mathbf{29.3480 \text{ J K}^{-1}}$$

SOLVED PROBLEM 22. The enthalpy change for the transition of liquid water to steam is 40.8 KJmol⁻¹ at 373 K. Calculate ΔG for the process.

SOLUTION :

Formula used

$$\Delta S_v = \frac{\Delta H_v}{T_b}$$

Quantities given

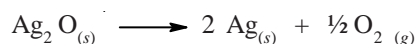
$$\Delta H_v = 40.8 \text{ kJ mol}^{-1} = 40800 \text{ J mol}^{-1}$$

$$T_b = 373 \text{ K}$$

Substitution of values

$$\begin{aligned} \Delta S_v &= \frac{40800 \text{ J mol}^{-1}}{373 \text{ K}} \\ &= \mathbf{109.38 \text{ J K}^{-1} \text{ mol}^{-1}} \end{aligned}$$

SOLVED PROBLEM 23. For the reaction



calculate the temperature at which free energy change is equal to zero. ΔH for the reaction is $+ 30.50 \text{ kJ mol}^{-1}$ and ΔS is $0.066 \text{ kJ K}^{-1} \text{ mol}^{-1}$ at 1 atm pressure. Predict the nature of the reaction (i) below this temperature and (ii) above this temperature.

SOLUTION :

Formula used

$$\Delta G = \Delta H - T\Delta S$$

$$[\because \Delta G = 0]$$

or

$$T = \frac{\Delta H}{\Delta S}$$

Quantities given

$$\Delta H = 30.50 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$\Delta S = 0.066 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

Substitution of values

$$\begin{aligned} T &= \frac{30.50 \text{ kJ mol}^{-1}}{0.066 \text{ kJ mol}^{-1} \text{ K}^{-1}} \\ &= 462 \text{ K} \end{aligned}$$

(i) At temperature below 463 K $\Delta H > T\Delta S$ and

$\therefore \Delta G = + \text{ve}$. The reaction is **non - spontaneous**

(ii) At temperature above 463 K $\Delta H < T\Delta S$ and

$\therefore \Delta G = - \text{ve}$. The reaction is **spontaneous**.

SOLVED PROBLEM 24. Calculate the entropy change for the following reversible processes :

(i) 1 mole of liquid water at 1 atm and at 100°C evaporates to 1 mole water vapour at 1 atm at 100°C

(ΔH_{vap} for $\text{H}_2\text{O} = 2257 \text{ J g}^{-1}$)

(ii) 1 mole of *a*-tin at 1 atm pressure and 13°C changes to 1 mole of *b*-tin at 1 atm and 13°C .

($\Delta H_{\text{transition}} (\text{Sn}) = 2090 \text{ J mol}^{-1}$)

SOLUTION :



Formula used

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_b}$$

Quantities given

$$\Delta H_v = 40.626 \text{ kJ mol}^{-1}$$

$$T_b = 373 \text{ K}$$

Substitution of values

$$\begin{aligned} \Delta S_{\text{vap}} &= \frac{40.626 \text{ kJ mol}^{-1}}{373 \text{ K}} \\ &= 108.916 \text{ JK}^{-1} \text{ mol}^{-1} \end{aligned}$$



Formula used

$$\Delta S_{\text{transition}} = \frac{\Delta H_{\text{transition}}}{T_{\text{transition}}}$$

Quantities given

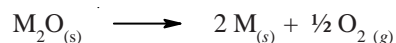
$$\Delta H_{\text{transition}} = 2090 \text{ J mol}^{-1}$$

$$T_{\text{transition}} = 13 + 273 = 286 \text{ K}$$

Substitution of values

$$\begin{aligned}\Delta S_{\text{transition}} &= \frac{2090 \text{ J mol}^{-1}}{286 \text{ K}} \\ &= 7.30 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

SOLVED PROBLEM 25. For the reaction



$\Delta H = 30 \text{ kJ mol}^{-1}$ and $\Delta S = 0.07 \text{ kJ K}^{-1} \text{ mol}^{-1}$ at 1 atm pressure. Calculate upto which temperature the reaction would not be spontaneous.

SOLUTION :

Formula used

$$\Delta G = \Delta H - T\Delta S$$

or

$$T = \frac{\Delta H}{\Delta S} \quad \left[\because \Delta G = 0 \right. \\ \left. \text{at Equilibrium} \right]$$

Quantities given

$$\Delta H = 30 \text{ kJ mol}^{-1}$$

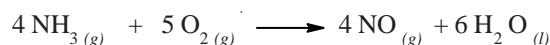
$$\Delta S = 0.07 \text{ kJ JK}^{-1} \text{ mol}^{-1}$$

Substitution of values

$$\begin{aligned}T &= \frac{30 \text{ kJ mol}^{-1}}{0.07 \text{ kJ K}^{-1} \text{ mol}^{-1}} \\ &= 428.57 \text{ K}\end{aligned}$$

Thus the reaction would not be spontaneous up to 428.57 K

SOLVED PROBLEM 26. Predict whether at 27 °C, the following reaction is spontaneous or not :



Given $\Delta H = +9080 \text{ J mol}^{-1}$ and $\Delta S = +35.7 \text{ JK}^{-1} \text{ mol}^{-1}$

SOLUTION :

Formula used

$$\Delta G = \Delta H - T\Delta S$$

Quantities given

$$\Delta H = 9080 \text{ J mol}^{-1}$$

$$T = 27 + 273 = 300 \text{ K}$$

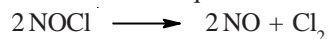
$$\Delta S = 35.7 \text{ J mol}^{-1} \text{ K}^{-1}$$

Substitution of values

$$\begin{aligned}\Delta G &= 9080 \text{ J mol}^{-1} - 300 \text{ K} \times 35.7 \text{ J mol}^{-1} \text{ K}^{-1} \\ &= 9080 \text{ J mol}^{-1} - 10710 \text{ J mol}^{-1} \\ &= -1630 \text{ J mol}^{-1}\end{aligned}$$

Since $\Delta G = -ve$, the reaction is spontaneous.

SOLVED PROBLEM 27. What is the equilibrium constant K for the reaction



at 27 °C if at this temperature ΔH and ΔS are 10 kJ mol^{-1} and $122 \text{ JK}^{-1} \text{ mol}^{-1}$ respectively ? ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)

SOLUTION :

(i) To calculate the value of ΔG

Formula used

$$\Delta G = \Delta H - T\Delta S$$

Quantities given

$$\Delta H = 70 \text{ kJ mol}^{-1} = 70000 \text{ J mol}^{-1}$$

$$T = 27 + 273 \text{ K} = 300 \text{ K}$$

$$\Delta S = 122 \text{ JK}^{-1} \text{ mol}^{-1}$$

Substitution of values

$$\begin{aligned}\Delta G &= 70000 \text{ J mol}^{-1} - 300 \text{ K} \times 122 \text{ J mol}^{-1} \\ &= 70000 \text{ J mol}^{-1} - 36600 \text{ J mol}^{-1} \\ &= 33400 \text{ J mol}^{-1}\end{aligned}$$

(ii) To calculate the equilibrium constant K**Formula used**

$$\Delta G = -2.303 R T \log K$$

Quantities given

$$\Delta G = 33400 \text{ J mol}^{-1}$$

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$T = 27 + 273 = 300 \text{ K}$$

Substitution of values

$$33400 \text{ J mol}^{-1} = -2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \times \log K$$

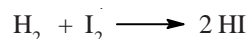
$$33400 \text{ J mol}^{-1} = -5744.14 \text{ J mol}^{-1} \times \log K$$

$$\begin{aligned}\text{or} \quad \log K &= - \frac{33400 \text{ J mol}^{-1}}{5744.14 \text{ J mol}^{-1}} \\ &= -5.8146\end{aligned}$$

$$\text{or} \quad K = \text{Antilog}(-5.8146)$$

$$\text{or} \quad K = 1.532 \times 10^{-6}$$

SOLVED PROBLEM 28. Calculate the equilibrium constant at 25 °C for the reaction



if standard free energy of formation of HI is $1.30 \text{ kJ mol}^{-1} \text{ mol}^{-1}$ ($R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)

SOLUTION :**(i) To calculate ΔG for the reaction**

$$\begin{aligned}\text{H}_2 + \text{I}_2 &\longrightarrow 2 \text{HI} \\ \Delta G^\circ &= \Delta G^\circ_{f(\text{products})} - \Delta G^\circ_{f(\text{Reactants})} \\ &= [2 \times \Delta G^\circ_{f(\text{HI})}] - [\Delta G^\circ_{f(\text{H}_2)} + \Delta G^\circ_{f(\text{I}_2)}] \\ &= 2 \times 1.30 \text{ kJ mol}^{-1} - [0 + 0] \\ &= 2.60 \text{ kJ mol}^{-1} \\ &= 2.60 \times 128 \text{ kJ} \quad [\because 1 \text{ mol}^{-1} = 128 \text{ g of HI}] \\ &= 332.8 \text{ kJ}\end{aligned}$$

(ii) To calculate the equilibrium constant K**Formula used**

$$\Delta G = -2.303 R T \log K$$

Quantities given

$$\Delta G = 332.8 \text{ kJ}$$

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1} = 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}$$

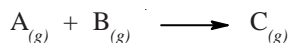
$$T = 25 + 273 = 298 \text{ K}$$

Substitution of values

$$332.8 \text{ kJ} = -2.303 \times 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \log K$$

$$\begin{aligned} \text{or} \quad \log K &= \frac{-332.8}{2.303 \times 8.314 \times 10^{-3} \times 298} \\ &= -5.833 \times 10^{-2+3} \\ &= -58.33 \end{aligned}$$

$$\begin{aligned} \text{or} \quad K &= \text{Antilog } -58.33 \\ &= 4.677 \times 10^{-59} \end{aligned}$$

SOLVED PROBLEM 29. For the reaction at 298 K

given that $\Delta E = -5 \text{ kcal}$ and $\Delta S = -10 \text{ cal K}^{-1}$. Calculate ΔG for the reaction and predict whether the reaction may occur spontaneously.

SOLUTION :**Formula used**

$$\Delta G = \Delta H - T\Delta S$$

$$\text{or} \quad \Delta G = \Delta E + \Delta n R T - T\Delta S \quad [\because \Delta H = \Delta E + \Delta n R T]$$

Quantities given

$$\Delta G = n_p - n_r = 1 - 2 = -1 \text{ mol}$$

$$\Delta E = -5 \text{ kcal} = -5000 \text{ cal}$$

$$R = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$T = 25 + 273 = 298 \text{ K}$$

Substitution of values

$$\begin{aligned} \Delta G &= -5000 \text{ cal} + (-1 \text{ mol}) \times 1.987 \text{ cal K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} - 298 \text{ K} (-10) \text{ cal} \\ &= -5000 \text{ cal} - 592.13 \text{ cal} + 2980 \text{ cal} \\ &= -2612.13 \text{ cal} \end{aligned}$$

Since ΔG is -ve, the reaction is spontaneous.

ADDITIONAL PRACTICE PROBLEMS

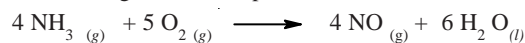
- Calculate the efficiency of steam engine operating between 100°C and 25°C . What would be the efficiency of the engine if the boiler temperature is raised to 150°C , the temperature of the sink remaining same?

Answer. 22.1% ; 29.55%

- Calculate the amount of the heat supplied to Carnot cycle working between 105°C and 20°C if the maximum work obtained is 200 cal?

Answer. 889.4 cal

- Predict whether at 27°C the following reaction is spontaneous or not :



Given $\Delta H = +9080 \text{ J mol}^{-1}$ and $\Delta S = +35.7 \text{ J K}^{-1} \text{ mol}^{-1}$.

Answer. Spontaneous

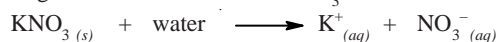
- Calculate entropy change for the reaction



if absolute entropies ($\text{JK}^{-1} \text{ mol}^{-1}$) are $A = 130$, $B = 203$ and $C = 152$

Answer. $225 \text{ J K}^{-1} \text{ mol}^{-1}$

- Calculate the free energy change for the dissociation of KNO_3 in water at 298 K



$$\Delta H^\circ = 34 \text{ kJ mol}^{-1}$$

$$\Delta S^\circ = 0.116 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

Answer. 568 J mol^{-1}

6. For the reaction $M_2O_{(s)} \longrightarrow 2M_{(s)} + \frac{1}{2}O_{2(g)} \Delta H = 30 \text{ kJ mol}^{-1}$ and $\Delta S = 0.07 \text{ kJ K}^{-1} \text{ mol}^{-1}$ (at 1 atm). Calculate up to which temperature reaction would not be spontaneous.
Answer. 428.57K
7. Ethanol boils at 78.4 °C and standard enthalpy of vaporisation of ethanol is 42. kJ mol⁻¹. Calculate the entropy of vaporisation of ethanol.
Answer. 120.66 JK⁻¹ mol⁻¹
8. At 0 °C, ice and water are in equilibrium and $\Delta H = 6.0 \text{ kJ mol}^{-1}$ for the process $H_2O_{(s)} \rightarrow H_2O_{(g)}$, calculate ΔS for the conversion of ice to fluid water.
Answer. 201.978 J mol⁻¹
9. What is the entropy change for conversion of one mole of ice to water at 273 K and 1 atm pressure (Given ΔH of ice = 6.025 kJ mol⁻¹).
Answer. 22.069 J mol⁻¹
10. For the reaction $2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{(g)}$ calculate ΔG at 700 K when enthalpy and entropy change ΔH and ΔS are - 113.0 kJ mol⁻¹ and - 145 JK⁻¹ mol⁻¹ respectively.
Answer. - 11.5 kJ mol⁻¹
11. For the reaction $Ag_2O_{(s)} \longrightarrow 2Ag_{(s)} + \frac{1}{2}O_{2(g)}$ calculate the temperature at which free energy change is equal to zero. [$\Delta H = 30.56 \text{ kJ mol}^{-1}$; $\Delta S = 0.066 \text{ kJ K}^{-1} \text{ mol}^{-1}$ at 1 atm pressure]
Answer. 462 K
12. At 373 K the entropy change for the transition of liquid water to steam is 109 JK⁻¹ mol⁻¹. Calculate the enthalpy change ΔH_{vap} for the process.
Answer. 40.657 kJ mol⁻¹
13. Calculate the entropy change ΔS° for the following reaction at 298K and 1 atm pressure.
- $$2CO_{(g)} + O_{2(g)} \longrightarrow 2CO_{2(g)}$$
- The absolute entropies (S°) at 298 K and 1 atm pressure are as follows :
- $$CO_{2(g)} = 213.6 \text{ J K}^{-1} \text{ mol}^{-1} \quad O_{2(g)} = 205.03 \text{ JK}^{-1} \text{ mol}^{-1} \quad CO_{(g)} = 197.6 \text{ JK}^{-1} \text{ mol}^{-1}$$
- Answer.** - 173.030 JK⁻¹ mol⁻¹
14. The enthalpy change for the transition of liquid water to steam (ΔH_{vap}) is 40.8 kJ mol⁻¹ at 373 K. Calculate the entropy change ΔS_{vap} for this process.
Answer. 109.38 JK⁻¹ mol⁻¹
15. The heat of vaporisation, ΔH_{vap} of carbon tetrachloride, CCl₄, at 25 °C is 43 kJ mol⁻¹. If 1 mole of liquid carbon tetrachloride at 25 °C has an entropy of 214 JK⁻¹, what is the entropy of 1 mole of the vapour in equilibrium with the liquid at this temperature ?
Answer. 358 JK⁻¹ mol⁻¹
16. If $\Delta G_f^\circ (MgO)$ is - 1361 kcal mol⁻¹ and $\Delta G_f^\circ (H_2O)$ is - 56.7 kcal mol⁻¹, calculate ΔG° of the reaction $MgO_{(s)} + H_{2(g)} \longrightarrow Mg_{(s)} + H_2O_{(l)}$ and predict whether the reaction is spontaneous or not.
Answer. 79.4 kcal ; No
17. The process $NH_{3(g)} + HCl_{(g)} \longrightarrow NH_4Cl_{(s)}$ is exothermic by -42.1 kcal at 1 atm and 25 °C. Find ΔG° for the reaction, given that $S^\circ_{NH_3} = + 46 \text{ cal mol}^{-1} \text{ K}^{-1}$; $S^\circ_{HCl} = + 44.6 \text{ cal K}^{-1} \text{ mol}^{-1}$ and $S^\circ_{NH_4Cl} = + 22 \text{ cal K}^{-1} \text{ mol}^{-1}$. Would the reaction be spontaneous ?
Answer. - 21.8 kcal ; Yes
18. The enthalpy change involved in oxidation of glucose is - 2880 kJ mol⁻¹. Twenty five percent of this energy is available for muscular work. If 100 kJ of muscular work is needed to walk one kilometer, what is the maximum distance a person will be able to walk after eating 120 g of glucose ?
Answer. 4.8 km

10

The Gaseous State and the Kinetic Molecular Theory

CHAPTER

KEY CONCEPTS AND EQUATIONS



THE GASEOUS STATE

All matter exist in three states gas, liquid and solid. The behaviour of gases is very important to a chemist. On account of their compressibility and thermal expansion, gases are affected by changes in pressure and temperature. The quantitative effect of change of pressure and temperature is described by Gas Laws.

PRESSURE

It is the force exerted by the impacts of the molecules of a gas per unit surface area. It is measured in **torr** or **mm Hg** or **atmosphere**. The SI unit of pressure is **Pascal (Pa)**.

$$1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ torr} = 1.013 \times 10^5 \text{ Pa}$$

TEMPERATURE

It is the degree of hotness or coldness of a gas. It determines the average kinetic energy of the gas molecules and is measured in **degrees Celsius**. The absolute temperature is measured in **degrees Kelvin**.

$$\text{K} = ^\circ\text{C} + 273$$

These two scales are represented in Fig 10.1.

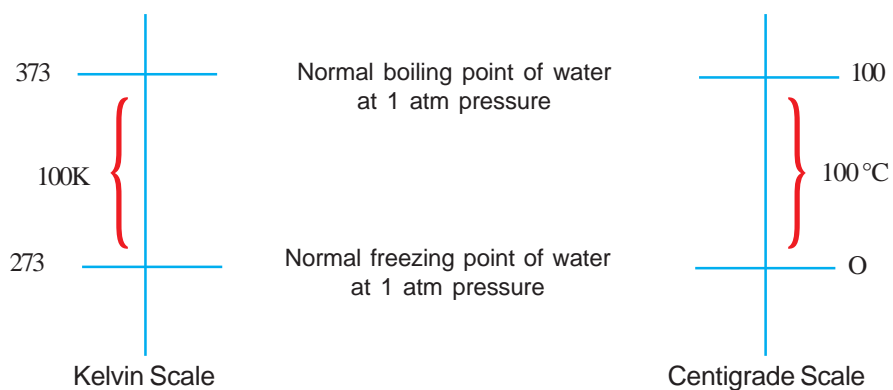


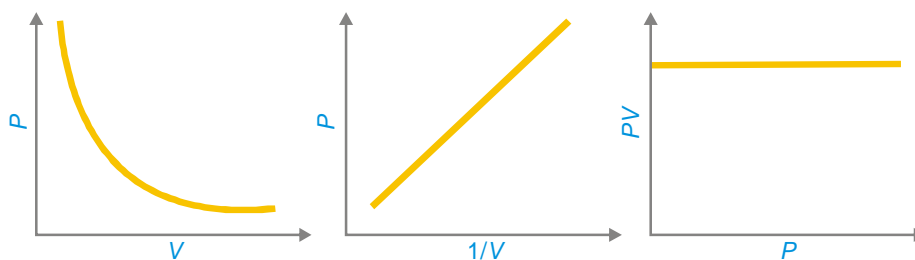
Figure 10.1
Comparison of Celsius and Kelvin Scales.

BOYLE'S LAW

The volume of a given sample of a gas varies **inversely** as its pressure at constant temperature. Mathematically, we can write

$$V \propto \frac{1}{P} \quad \text{or} \quad V = \frac{k}{P} \quad \text{or} \quad PV = k \quad (\text{At constant Temperature})$$

Graphically Boyle's law can be expressed in the following ways :



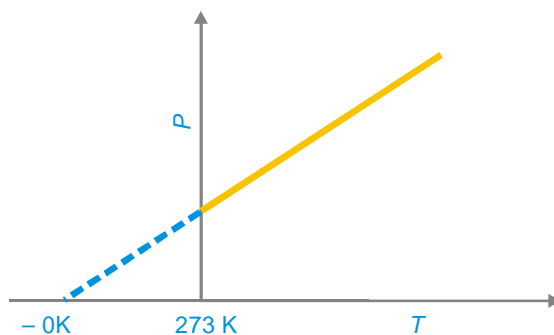
■ **Figure 10.2**
Graphical representation of Boyle's law.

CHARLE'S LAW

The volume of a given sample of a gas is **directly** proportional to its Kelvin or absolute temperature at constant pressure. Mathematically, we can write

$$V \propto T \quad \text{or} \quad V = kT \quad \text{or} \quad \frac{V}{T} = k \quad (\text{At constant pressure})$$

Graphically, Charles's law can be represented as



■ **Figure 10.3**
Graphical representation of Charles's law.

ABSOLUTE ZERO

The volume of the gas theoretically becomes zero at -273°C or 0 K and this *imaginary* temperature is called **absolute zero** of temperature. In actual practice, the gas changes to liquid or solid before this temperature is attained.

STANDARD CONDITIONS OF TEMPERATURE AND PRESSURE (STP)

The volume of gases present in two different samples can be compared only if these are at same temperature and pressure. For this purpose it is useful to adopt a set of standard conditions of temperature and pressure. By universal agreement, the standard temperature is chosen as 273 K (0°C) and the standard pressure as exactly as one atm (760 torr). These conditions of temperature and pressure are referred to as **Standard conditions** or **Standard temperature and pressure (STP)**.

AVOGADRO'S LAW

Equal volumes of all gases at same temperature and pressure contain equal number of molecules or moles. Mathematically,

$$V \propto n \quad \text{or} \quad V = A \times n \quad (T \text{ and } P \text{ constant})$$

where A is a constant of proportionality.

For two gases we have

$$n_1 = n_2 \quad \text{if} \quad V_1 = V_2 \quad (T \text{ and } P \text{ constant})$$

COMBINED GAS LAWS OR IDEAL GAS EQUATION

The simultaneous effect of change of pressure and temperature of a gas can be studied by combining Boyle's law and Charles' law. The derived new equation is called combined gas law or ideal gas equation.

$$\text{Boyle's law} \quad V \propto \frac{1}{P} \quad (T \text{ constant})$$

$$\text{Charles' law} \quad V \propto T \quad (P \text{ constant})$$

$$\therefore \quad V \propto \frac{T}{P}$$

$$\text{or} \quad V = \frac{kT}{P} \quad \text{or} \quad \frac{PV}{T} = k$$

$$\text{or} \quad \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

This expression is a mathematical statement of combined gas law. If $T_1 = T_2$, the equation reduces to $P_1 V_1 = P_2 V_2$ (Boyle's law). Alternatively, if $P_1 = P_2$ the expression becomes $V_1/T_1 = V_2/T_2$ (Charles' law)

THE GAS CONSTANT, R

Besides temperature and pressure, the volume of a gas depends upon the number of moles of the gas. Therefore, the constant k in the combined gas law can be regarded as a product of two factors, one of which is the number of moles of the gas. Therefore, we can write

$$\frac{PV}{T} = k \quad \text{or} \quad \frac{PV}{T} = nR$$

where n is the number of moles of gas and R is a new constant called gas constant. Its value depends upon the units in which P , V and T are expressed.

$$\begin{aligned} R &= 8.314 \text{ JK}^{-1} \text{ mol}^{-1} = 8.314 \times 10^7 \text{ ergs K}^{-1} \text{ mol}^{-1} \\ &= 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1} \end{aligned}$$

SOLVING NUMERICAL PROBLEMS ON IDEAL GAS EQUATION

In numerical problems related to ideal gas equation, there are four variables (P , V , T and n). Out of these four, three are generally given and the value of fourth is to be calculated. The temperature must be expressed in absolute temperature scale (in Kelvins). The units of P and V are generally in atmosphere and litre (dm^3). If other units are given for pressure and volume, convert them to atmosphere and litre (dm^3) respectively and use $R = 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1}$.

DALTON'S LAW OF PARTIAL PRESSURES

The total pressure of a mixture of non-reacting gases is equal to the sum of their partial pressures. Mathematically,

$$P_{Total} = P_A + P_B + P_C + \dots \quad (V \text{ and } T \text{ are constant})$$

where p_A, p_B, p_C, \dots etc. are the partial pressures of gases A, B, C, respectively. The ideal gas equation $P V = n R T$ can be applied to each gas separately and we can write.

$$p_A = n_A \frac{RT}{V} \quad p_B = n_B \frac{RT}{V} \quad p_C = n_C \frac{RT}{V}$$

where n_A, n_B and n_C are number of moles of gases A, B and C respectively. The total pressure of gaseous mixture is

$$\begin{aligned} P_{Total} &= n_A \frac{RT}{V} + n_B \frac{RT}{V} + n_C \frac{RT}{V} + \dots \\ &= (n_A + n_B + n_C + \dots) \frac{RT}{V} \\ &= n_{Total} \frac{RT}{V} \end{aligned}$$

GRAHAM'S LAW OF DIFFUSION

The rate of diffusion of a gas is inversely proportional to the square root of its density. Mathematically,

$$r \propto \sqrt{\frac{1}{d}}$$

For two gases A and B, under identical conditions

$$\frac{r_A}{r_B} = \sqrt{\frac{d_B}{d_A}}$$

or in terms of molecular masses

$$\frac{r_A}{r_B} = \sqrt{\frac{\text{molecular mass of gas B}}{\text{molecular mass of gas A}}} \quad [\because VD = 2 \times \text{Mol. mass}]$$

THE MOLAR GAS VOLUME

The volume occupied by one mole of a gas at standard temperature and pressure is its molar volume. At STP one mole of a gas occupies volume equal to 22.4 lit (or dm^3) i.e.

Volume of one mole of a gas at STP = 22.4 litre.

RELATIONSHIPS DERIVED FROM KINETIC MOLECULAR THEORY OF GASES

If N molecules of a gas, each of mass m are enclosed in a container of volume V , the pressure exerted by the gas molecules derived from kinetic molecular theory is related by the equation

$$PV = \frac{1}{3} m N \mu^2$$

where μ is the **root mean square velocity**. It is defined as the imaginary velocity when all the gas molecules would possess if the total kinetic energy is equally divided among them. For n molecules having velocities v_1, v_2, v_3, \dots , the root mean square velocity is given by

$$\mu = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + \dots}{N}}$$

$$= \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{D}} \quad \left[\because \begin{matrix} RT = PV \text{ and} \\ M/V = D \end{matrix} \right]$$

The **average velocity** is given by

$$\begin{aligned} \bar{v} &= \frac{v_1 + v_2 + v_3 + \dots}{N} \\ &= \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8PV}{\pi M}} = \sqrt{\frac{8P}{D}} \end{aligned}$$

The **most probable velocity** is the velocity possessed by maximum number of molecules of a gas. It is given by

$$\mu_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2PV}{M}} = \sqrt{\frac{2P}{D}}$$

RELATION BETWEEN AVERAGE VELOCITY, ROOT MEAN SQUARE VELOCITY AND MOST PROBABLE VELOCITY

$$\begin{aligned} \bar{v} : \mu : \mu_{mp} &= \sqrt{\frac{8RT}{\pi M}} : \sqrt{\frac{3RT}{M}} : \sqrt{\frac{2RT}{M}} \\ &= 1.128 : 1.224 : 1 \end{aligned}$$

AVERAGE KINETIC ENERGY OF A GAS

The kinetic molecular gas equation is

$$PV = \frac{1}{3} m N \mu^2 = \frac{2}{3} N \times \frac{1}{2} m \mu^2 = \frac{2}{3} N \times e$$

where e is the average kinetic energy of a single molecule

$$\text{or } PV = \frac{2}{3} E \quad \text{or } nRT = \frac{2}{3} E \quad \text{or } E = \frac{3}{2} nRT$$

where E is the total kinetic energy of N molecules.

COLLISION PROPERTIES

Mean Free Path

The mean distance travelled by a molecule between two successive collisions is the mean free path. It is related to the coefficient of viscosity of the gas by the relation

$$\lambda = \eta \sqrt{\frac{3}{PD}}$$

where P is the pressure of the gas, D the density and η the coefficient of viscosity of the gas.

Collision Frequency

The number of molecular collisions taking place per second per unit volume of the gas is called collision frequency. It is denoted by Z and is given by the relation.

$$Z = \frac{\pi \bar{v} \sigma^2 \bar{N}^2}{\sqrt{2}}$$

where \bar{v} is the average velocity, σ the molecular diameter and \bar{N} the number of molecules of the gas per cm^3 .

MOLAR HEAT CAPACITIES OF IDEAL GASES

Specific Heat

It is the amount of heat required to raise the temperature of one gram of a substance through 1°C .

Molar Heat Capacity

It is the amount of heat required to raise the temperature of one mole of a gas through 1°C . Thus

$$\text{Molar Heat Capacity} = \text{Specific heat} \times \text{molecular mass of the gas}$$

Molar Heat Capacity at constant volume (C_v)

It is the amount of heat required to raise the temperature of one mole of a gas at constant volume.

Molar Heat Capacity at constant pressure (C_p)

It is the amount of heat required to raise the temperature of one mole of a gas at constant pressure. It has been found that $C_p > C_v$ and the difference between the two is equal to the gas constant *i.e.*

$$C_p - C_v = R = 1.987 \text{ cal}$$

Specific Heat Ratio

The ratio C_p/C_v , denoted by the symbol γ , which varies with the atomicity of the gas.

For a monoatomic gas $C_p = \frac{5}{2}R$; $C_v = \frac{3}{2}R$
 and $\gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = 1.667$

For a diatomic gas $C_p = \frac{7}{2}R$; $C_v = \frac{5}{2}R$
 and $\gamma = \frac{C_p}{C_v} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = 1.40$

For polyatomic gas $C_p = \frac{8}{2}R$; $C_v = \frac{6}{2}R$
 and $\gamma = \frac{C_p}{C_v} = \frac{\frac{8}{2}R}{\frac{6}{2}R} = 1.33$

REAL GASES : VANDER WAALS EQUATION

An ideal gas is one which obeys the gas laws and the gas equation ($PV = nRT$) at all pressures and temperatures. However, no gas is ideal. Almost all gases show deviations from the ideal behaviour and are called real gases. The extent to which is real gas departs from ideal behaviour is given by a factor called compressibility factor Z , given by

$$Z = \frac{PV}{RT}$$

For ideal gases $Z = 1$ and for real gas $Z < 1$ or $Z > 1$. The gases under high pressures and low temperatures deviate from the ideal behaviour. The deviations from ideality is due to faulty assumptions of the kinetic molecular theory. These are

- (i) the molecules in a gas possess no volume
- (ii) there are no intermolecular forces among the molecules of a gas.

vander Waals modified the gas equation and the new equation is vander Waals equation

$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

where the factors $\frac{n^2 a}{V^2}$ and nb are the pressure and volume correction factors respectively. These factors account for the inter molecular attractive forces and the actual volume occupied by the gas molecules. 'a' and 'b' are constants called vander Waals constants.

Units of 'a' and 'b'

The units of vander Waals constants are

$$a = \text{atm lit}^2 \text{ mol}^{-2} \quad \text{or} \quad \text{kPa dm}^3 \text{ mol}^{-1}$$

$$\text{and} \quad b = \text{lit mol}^{-1} \quad \text{or} \quad \text{dm}^3 \text{ mol}^{-1}$$

The vander Waals constant 'b' is four times the actual volume of the gas molecule *i.e.*

$$b = 4 \times \text{Avogadro's number} \times \frac{4}{3} \pi r^3$$

where r is the radius of the gas molecule.

CRITICAL PHENOMENON

Critical Temperature (T_c) of a gas is that temperature above which it cannot be liquified no matter how great the pressure applied.

Critical Pressure (P_c) of a gas is the minimum pressure required to liquify a gas at its critical temperature.

Critical Volume (V_c) of a gas is the volume occupied by one mole of it at its critical temperature and critical pressure.

Relations between Critical Constants and vander Waals constants

$$V_c = 3b \quad P_c = \frac{a}{27b^2} \quad T_c = \frac{8a}{27Rb}$$

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. At what temperature would ethane molecules have the same root mean square velocity as methane molecules at 27°C .

SOLUTION :**Formula used**

$$\mu = \sqrt{\frac{3RT}{M}}$$

Quantities given

$$T = 27 + 273 = 300 \text{ K}$$

$$\text{mol. mass of CH}_4 = 16$$

$$\text{mol mass of C}_2\text{H}_6 = 30$$

Substitution of values

$$\mu_{\text{CH}_4} = \sqrt{\frac{3R \times 300}{16}} = \sqrt{\frac{900R}{16}}$$

and

$$\mu_{\text{C}_2\text{H}_6} = \sqrt{\frac{3R \times 300}{30}} = \sqrt{\frac{3RT}{30}}$$

Since two velocities are equal, we have

$$\sqrt{\frac{900R}{16}} = \sqrt{\frac{3RT}{30}}$$

Squaring both sides

$$\frac{900R}{16} = \frac{3RT}{30}$$

or

$$\begin{aligned} T &= \frac{900 \times 30}{16 \times 3} \text{ K} \\ &= 562.5 \text{ K} \\ &= 562.5 - 273^\circ\text{C} \\ &= \mathbf{289.5^\circ\text{C}} \end{aligned}$$

SOLVED PROBLEM 2. Calculate the root mean square velocity of oxygen molecules at 27 °C.

SOLUTION :

Formula used

$$\mu = \sqrt{\frac{3RT}{M}}$$

Quantities given

$$T = 27 + 273 = 300 \text{ K}$$

$$R = 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$$

$$M = 32 \text{ g mol}^{-1}$$

Substitution of values

$$\begin{aligned} \mu_{o_2} &= \sqrt{\frac{3 \times 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{32 \text{ g mol}^{-1}}} \\ &= \sqrt{23.383 \times 10^8 \text{ cm sec}^{-1}} \\ &= 4.8356 \times 10^4 \text{ cm sec}^{-1} \end{aligned}$$

SOLVED PROBLEM 3. Calculate the critical constants V_c , P_c and T_c for C_2H_2 using vander Waals constants $a = 4.390 \text{ atm lit mol}^{-2}$; $b = 0.05136 \text{ lit mol}^{-1}$ ($R = 0.082 \text{ atm lit K}^{-1} \text{ mol}^{-1}$)

SOLUTION :

(i) To calculate V_c

Formula used

$$V_c = 3b$$

Quantity given

$$b = 0.05136 \text{ lit mol}^{-1}$$

Substitution of values

$$V_c = 3 \times 0.05136 \text{ lit mol}^{-1} = 0.15408 \text{ lit}$$

(ii) To calculate P_c

Formula used

$$P_c = \frac{a}{27b^2}$$

Quantities given

$$a = 4.390 \text{ atm lit}^2 \text{ mol}^{-2}$$

$$b = 0.05136 \text{ lit mol}^{-1}$$

Substitution of values

$$\begin{aligned} P_c &= \frac{4.390 \text{ atm lit}^2 \text{ mol}^{-2}}{27 \times (0.05136 \text{ lit mol}^{-1})^2} \\ &= \frac{4.390}{27 \times 0.002638} \\ &= 61.64 \text{ atm} \end{aligned}$$

(iii) To calculate T_c

Formula used

$$T_c = \frac{8a}{27R}$$

Quantities given

$$a = 4.390 \text{ atm lit}^2 \text{ mol}^{-2}$$

$$R = 0.082 \text{ atm lit K}^{-1} \text{ mol}^{-1}$$

Substitution of values

$$\begin{aligned} T_c &= \frac{8 \times 4.390 \text{ atm lit}^2 \text{ mol}^{-2}}{27 \times 0.082 \text{ atm lit K}^{-1} \text{ mol}^{-1}} \\ &= 15.86 \text{ K} \end{aligned}$$

SOLVED PROBLEM 4. Calculate the root mean square velocity of oxygen molecules at 25 °C.

SOLUTION :

Formula used

$$\mu = \sqrt{\frac{3RT}{M}}$$

Quantities given

$$R = 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$$

$$T = 25 + 273 = 298 \text{ K}$$

$$M = 32 \text{ g mol}^{-1}$$

Substitution of values

$$\begin{aligned} \mu_{O_2} &= \sqrt{\frac{3 \times 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{32 \text{ g mol}^{-1}}} \\ &= \sqrt{23.227 \times 10^8 \text{ cm sec}^{-1}} \\ &= 4.819 \times 10^4 \text{ cm sec}^{-1} \end{aligned}$$

SOLVED PROBLEM 5. Calculate the root mean square velocity of CO₂ at 27 °C.

SOLUTION :

Formula used

$$\mu = \sqrt{\frac{3RT}{M}}$$

Quantities given

$$R = 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$$

$$T = 27 + 273 = 300 \text{ K}$$

$$M = 44 \text{ g mol}^{-1}$$

Substitution of values

$$\begin{aligned} \mu_{CO_2} &= \sqrt{\frac{3 \times 8.314 \times 10^7 \text{ erg K}^{-1} \times 300 \text{ K}}{44 \text{ g mol}^{-1}}} \\ &= \sqrt{17.059 \times 10^8 \text{ cm sec}^{-1}} \\ &= 4.130 \text{ cm sec}^{-1} \end{aligned}$$

SOLVED PROBLEM 6. One mole of diethyl ether occupies 15 litres at 227 °C. Calculate the pressure if vander Waals constants for diethyl ether are $a = 17.38 \text{ atm lit}^2 \text{ mol}^{-2}$ and $b = 0.134 \text{ lit mol}^{-1}$.

SOLUTION :

Formula used

$$\left(P + \frac{n^2 a}{V^2}\right) (V - nb) = nRT$$

or

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

Quantities given

$$n = 1 \text{ mol}$$

$$V = 15 \text{ lit}$$

$$R = 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1}$$

$$a = 17.38 \text{ atm lit}^2 \text{ mol}^{-2}$$

$$T = 500 \text{ K}$$

$$b = 0.134 \text{ lit mol}^{-1}$$

Substitution of values

$$\begin{aligned} P &= \frac{1 \text{ mol} \times 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 500 \text{ K}}{15 \text{ lit} - 0.134 \text{ lit}} - \frac{(1 \text{ mol})^2 \times 17.38 \text{ atm lit}^2 \text{ mol}^{-2}}{(15 \text{ lit})^2} \\ &= 2.795 \text{ atm} - 0.07724 \text{ atm} \\ &= 2.723 \text{ atm.} \end{aligned}$$

SOLVED PROBLEM 7. Calculate the root mean square velocity for oxygen molecules at 26.85 °C, given that the gas constant is $8.314 \times 10^7 \text{ erg mol}^{-1} \text{ deg}^{-1}$.

SOLUTION :

Formula used

$$\mu = \sqrt{\frac{3RT}{M}}$$

Quantities given

$$R = 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$$

$$T = 273.15 + 26.85 = 300\text{K}$$

$$M = 32 \text{ g mol}^{-1}$$

Substitution of values

$$\begin{aligned}\mu_{O_2} &= \sqrt{\frac{3 \times 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1} \times 300\text{K}}{32 \text{ g mol}^{-1}}} \\ &= \sqrt{23.383 \times 10^8 \text{ cm sec}^{-1}} \\ &= 4.8356 \times 10^4 \text{ cm sec}^{-1}\end{aligned}$$

SOLVED PROBLEM 8. A vessel of volume 1.0 litre contains 10^{25} gas molecules of mass 10^{-24} g each. If r. m. s. velocity is 10^5 cm sec^{-1} , calculate the total kinetic energy and temperature.

SOLUTION : (i) To calculate the total Kinetic energy

Formula used

$$K.E. = \frac{1}{2} m v^2$$

Quantities given

$$\begin{aligned}\text{Mass of the gas} &= \text{no. of molecules} \times \text{mass of each molecule} \quad v = 10^5 \text{ cm sec}^{-1} \\ &= 10^{25} \times 10^{-24} \text{ g} \\ &= 10 \text{ g}\end{aligned}$$

Substitution of values

$$\begin{aligned}\text{K.E. of the gas} &= \frac{1}{2} \times 10 \text{ g} \times (10^5 \text{ cm sec}^{-1})^2 \\ &= 5 \times 10^{10} \text{ ergs}\end{aligned}$$

(ii) To calculate the Temperature

Formula used

$$K.E. = \frac{3}{2} RT \text{ or } T = \frac{2K.E.}{3R}$$

Quantities given

$$K.E. = 5 \times 10^{10} \text{ ergs}$$

$$R = 8.314 \times 10^7 \text{ ergs K}^{-1} \text{ mol}^{-1}$$

Substitution of values

$$\begin{aligned}T &= \frac{2 \times 5 \times 10^{10} \text{ erg}}{3 \times 8.314 \times 10^7 \text{ ergs K}^{-1} \text{ mol}^{-1}} \\ &= 400.93 \text{ K} \\ &= 400.93 - 273 \text{ }^\circ\text{C} \\ &= 127.93 \text{ }^\circ\text{C}\end{aligned}$$

SOLVED PROBLEM 9. Critical density of a substance having molecular weight 111 is 0.555 g cm^{-3} and $P_c = 48 \text{ atm}$. Calculate the vander Waals constant 'a' and 'b'.

SOLUTION :

(i) To calculate 'b'

Formula used

$$V_c = 3b \text{ or } b = \frac{V_c}{3}$$

Quantities given

$$\text{Critical volume} = \frac{\text{Molecular mass}}{\text{Critical density}} = \frac{111 \text{ g mol}^{-1}}{0.555 \text{ g ml}^{-1}} = 200 \text{ ml mol}^{-1} = 0.2 \text{ lit mol}^{-1}$$

Substitution of values

$$b = \frac{0.2 \text{ lit mol}^{-1}}{3} = \mathbf{0.066 \text{ lit mol}^{-1}}$$

(ii) To calculate 'a'**Formula used**

$$P_c = \frac{a}{27 b^2} \quad \text{or} \quad a = 27 b^2 P_c$$

Quantities given

$$b = 0.066 \text{ lit mol}^{-1}$$

$$P_c = 48 \text{ atm}$$

Substitution of values

$$\begin{aligned} a &= 27 \times (0.066 \text{ lit mol}^{-1})^2 \times 48 \text{ atm} \\ &= \mathbf{5.645 \text{ atm lit}^2 \text{ mol}^{-2}} \end{aligned}$$

SOLVED PROBLEM 10. For ammonia gas vander Waals constants a and b are $4.0 \text{ litre}^2 \text{ atm}$ and $0.036 \text{ litre mol}^{-1}$ respectively. Calculate the critical volume ($R = 0.082 \text{ lit atm K}^{-1}$)

SOLUTION :**Formula used**

$$V_c = 3b$$

Quantity given

$$b = 0.036 \text{ lit mol}^{-1}$$

Substitution of values

$$\begin{aligned} V_c &= 3 \times 0.036 \times \text{lit mol}^{-1} \\ &= \mathbf{0.108 \text{ lit}} \end{aligned}$$

SOLVED PROBLEM 11. Calculate the pressure developed in a 5 litre vessel containing 88 g of CO_2 at 27°C . Assume CO_2 as van der Waals gas ($\text{C} = 12, \text{O} = 16$); $a = 3.59 \text{ atm lit}^2 \text{ mol}^{-2}$; $b = 0.043 \text{ lit mol}^{-1}$.

SOLUTION :**Formula used**

$$\left(P + \frac{n^2 a}{V^2} \right) (V - nb) = nRT$$

or

$$P = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

Quantities given

$$n = \frac{88 \text{ g}}{44 \text{ g mol}^{-1}} = 2 \text{ mole}$$

$$R = 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1}$$

$$V = 5 \text{ lit}$$

$$T = 27 + 273 = 300 \text{ K}$$

$$a = 3.59 \text{ atm lit}^2 \text{ mol}^{-2}$$

$$b = 0.043 \text{ lit mol}^{-1}$$

Substitution of values

$$\begin{aligned} P &= \frac{2 \text{ mol} \times 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{5 \text{ lit} - 2 \times 0.043 \text{ lit}} - \frac{(2 \text{ mol})^2 \times 3.59 \text{ atm lit}^2 \text{ mol}^{-2}}{(5 \text{ lit})^2} \\ &= \frac{49.26}{4.914} \text{ atm} - 0.574 \text{ atm} \\ &= \mathbf{9.450 \text{ atm}} \end{aligned}$$

SOLVED PROBLEM 12. If for a gas $T_c = 31^\circ\text{C}$, $P_c = 72.8 \text{ atm}$ and $R = 0.082$ then calculate the vander Waals constant a and b .

SOLUTION :**(i) To calculate 'b'****Formula used**

$$P_c = \frac{a}{27 b^2} \quad \text{and} \quad T_c = \frac{8 a}{27 R b}$$

or $\frac{P_c}{T_c} = \frac{a}{27 b^2} \times \frac{27 R b}{8 a} = \frac{R}{8 b}$

or $b = \frac{R T_c}{8 P_c}$

Quantities given

$$T_c = 31 + 273 = 304 \text{ K}$$

$$P_c = 72.8 \text{ atm}$$

$$R = 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1}$$

Substitution of values

$$b = \frac{0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 304 \text{ K}}{8 \times 72.8 \text{ atm}}$$

$$= 0.04285 \text{ lit mol}^{-1}$$

(ii) To calculate 'a'**Formula used**

$$P_c = \frac{a}{27 b^2} \quad \text{or} \quad a = 27 P_c b^2$$

Quantities given

$$P_c = 72.8 \text{ atm}$$

$$b = 0.04285 \text{ lit mol}^{-1}$$

Substitution of values

$$a = 27 \times 72.8 \text{ atm} \times (0.04285 \text{ lit mol}^{-1})^2$$

$$= 3.6091 \text{ atm lit}^2 \text{ mol}^{-1}$$

SOLVED PROBLEM 13. Calculate the root mean square, velocity, average velocity and the most probable velocity of a gas at 27 °C, where the mass of gas molecule is 4.4688×10^{-26} kg.

SOLUTION :**(i) To calculate the molecular mass of the gas**

$$\begin{aligned} \text{Mass of a molecule of the gas} &= 4.4688 \times 10^{-26} \text{ kg} \\ &= 4.4688 \times 10^{-23} \text{ g} \end{aligned}$$

$$\begin{aligned} \text{Molecular mass} &= \text{Avogadro's number} \times \text{Mass of one molecule} \\ &= 6.023 \times 10^{23} \text{ mol}^{-1} \times 4.4688 \times 10^{-23} \text{ g} \\ &= 26.90 \text{ g mol}^{-1} \end{aligned}$$

(ii) To calculate the root mean square velocity**Formula used**

$$\mu = \sqrt{\frac{3 R T}{M}}$$

Quantities given

$$R = 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$$

$$T = 27 + 273 = 300 \text{ K}$$

$$M = 26.90 \text{ g mol}^{-1}$$

Substitution of values

$$\mu = \sqrt{\frac{3 \times 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{26.90 \text{ g mol}^{-1}}}$$

$$= \sqrt{27.816 \times 10^8}$$

$$= 5.274 \times 10^4 \text{ cm sec}^{-1}$$

(ii) To calculate the average velocity

$$v = 0.9213 \times \mu$$

$$= 0.9213 \times 5.274 \times 10^4 \text{ cm sec}^{-1}$$

$$= 4.859 \times 10^4 \text{ cm sec}^{-1}$$

(iii) To calculate the most probable velocity

$$\mu_{mp} = \sqrt{\frac{2}{3}} \times \mu$$

$$= \sqrt{\frac{2}{3}} \times 5.274 \times 10^4 \text{ cm sec}^{-1}$$

$$= 4.306 \times 10^4 \text{ cm sec}^{-1}$$

SOLVED PROBLEM 14. vander Walls constants for CO_2 are $a = 3.65 \times 10^{-1} \text{ Nm}^4 \text{ mol}^{-2}$, $b = 4.28 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$. Calculate T_c and V_c of the gas.

SOLUTION :

(i) To calculate 'b'

Formula used

$$V_c = 3b$$

Quantity given

$$b = 4.28 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

Substitution of values

$$V_c = 3 \times 4.28 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

$$= 1.284 \times 10^{-4} \text{ m}^3$$

(ii) To calculate 'a'

Formula used

$$T_c = \frac{8a}{27Rb}$$

Quantities given

$$a = 3.65 \times 10^{-1} \text{ Nm}^4 \text{ mol}^{-2} \quad R = 8.314 \text{ Nm K}^{-1} \text{ mol}^{-1} \quad b = 4.28 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

Substitution of values

$$T_c = \frac{8 \times 3.65 \times 10^{-1} \text{ Nm}^4 \text{ mol}^{-2}}{27 \times 8.314 \text{ Nm K}^{-1} \text{ mol}^{-1} \times 4.28 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}}$$

$$= 303.92 \text{ K}$$

SOLVED PROBLEM 15. Calculate the root mean square velocity of nitrogen at 27°C and 700 mm pressure.

SOLUTION :

(i) To convert Gram molar volume to given conditions

$$\text{At NTP} \quad P_1 = 760 \text{ mm} \quad V_1 = 22400 \text{ ml} \quad T_1 = 273 \text{ K}$$

$$\text{At given conditions} \quad P_2 = 700 \text{ mm} \quad T_2 = 300 \text{ K}$$

Formula used

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \text{or} \quad V_2 = \frac{P_1 V_1 T_2}{T_1 P_2}$$

Substitution of values

$$\begin{aligned} V_2 &= \frac{760 \text{ mm} \times 22400 \text{ ml} \times 300 \text{ K}}{273 \text{ K} \times 700 \text{ mm}} \\ &= 26725 \text{ ml} \end{aligned}$$

(ii) To calculate root mean square velocity, μ **Formula used**

$$\mu = \sqrt{\frac{3PV}{M}}$$

Quantities given

$$V = 26725 \text{ ml} \quad P = 700 \text{ mm Hg} = 70 \text{ cm of Hg} = 70 \times 13.6 \times 981 \quad M = 28 \text{ g mol}^{-1}$$

Substitution of values

$$\begin{aligned} \mu &= \sqrt{\frac{3 \times 70 \times 13.6 \times 981 \times 26725}{28}} \\ &= 51712 \text{ cm sec}^{-1} \\ &= 5.1712 \times 10^4 \text{ cm sec}^{-1} \end{aligned}$$

SOLVED PROBLEM 16. Calculate the root mean square speed of CO_2 Molecules at 27°C .**SOLUTION :****Formula used**

$$\mu = \sqrt{\frac{3RT}{M}}$$

Quantities given

$$R = 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1} \quad T = 27 + 273 = 300 \quad M = 44 \text{ g mol}^{-1}$$

Substitution of values

$$\begin{aligned} \mu &= \sqrt{\frac{3 \times 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{44 \text{ g mol}^{-1}}} \\ &= \sqrt{17.0059 \times 10^8} \\ &= 4.1238 \text{ cm sec}^{-1} \end{aligned}$$

SOLVED PROBLEM 17. What would be the pressure exerted by 0.8 mole of NO_2 in a vessel of Volume 20 dm^3 at 300 K from vander Waals equation. ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, $a = 0.535 \text{ Nm}^4 \text{ mol}^{-2}$, $b = 4.42 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$).

SOLUTION :**Formula used**

$$\left(P + \frac{a n^2}{V^2} \right) (V - n b) = n R T$$

or

$$P = \frac{n R T}{V - n b} - \frac{a n^2}{V^2}$$

Quantities given

$$\begin{aligned} n &= 0.8 \text{ mole} & R &= 8.314 \text{ J K}^{-1} \text{ mol}^{-1} & V &= 20 \text{ dm}^3 = 0.02 \text{ m}^3 \\ T &= 300 \text{ K} & a &= 0.535 \text{ Nm}^4 \text{ mol}^{-2} & b &= 4.42 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1} \end{aligned}$$

Substitution of values

$$\begin{aligned}
 P &= \frac{0.8 \text{ mol} \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{0.02 \text{ m}^3 - 0.8 \text{ mol} \times 4.42 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}} - \frac{0.535 \text{ Nm}^4 \text{ mol}^{-2} \times (0.8 \text{ mol})^2}{(0.02 \text{ m}^3)^2} \\
 &= \frac{1995.36}{0.01996} \text{ Nm}^{-2} - 858.6 \text{ Nm}^{-2} \\
 &= 99088 \text{ Nm}^{-2} \\
 &= \frac{99088}{1.01325 \times 10^5} \text{ atm} \quad [\because 1 \text{ atm} = 1.01325 \times 10^5 \text{ Nm}^{-2}] \\
 &= \mathbf{0.9779 \text{ atm}}
 \end{aligned}$$

SOLVED PROBLEM 18. Calculate the mean free path for oxygen molecule at 300 K and pressure 101.325 k Pa. The collision diameter of oxygen molecule is 0.362 nm. (Avogadro's number $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$).

SOLUTION :**(i) To calculate the number of molecules of oxygen per unit volume****Formula used**

$$\bar{n} = \frac{P}{RT} \times N$$

Quantities given

$$P = 101.325 \text{ kPa} = 101325 \text{ Pa}$$

$$T = 300 \text{ K}$$

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$N = 6.023 \times 10^{23} \text{ mol}^{-1}$$

Substitution of values

$$\begin{aligned}
 \bar{n} &= \frac{101325 \text{ Pa} \times 6.023 \times 10^{23} \text{ mol}^{-1}}{8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 300 \text{ K}} \\
 &= 2.44679 \times 10^{25} \text{ m}^{-3}
 \end{aligned}$$

(ii) To calculate the mean free path**Formula used**

$$L = \frac{1}{\sqrt{2} \times \pi \sigma^2 \bar{n}}$$

Quantities given

$$\sigma = 0.362 \text{ nm} = 0.362 \times 10^{-9} \text{ m}$$

$$\bar{n} = 2.44679 \times 10^{25} \text{ m}^{-3}$$

Substitution of values

$$\begin{aligned}
 L &= \frac{1}{\sqrt{2} \times 3.14 \times (0.362 \times 10^{-9} \text{ m})^2 \times (2.44679 \times 10^{25} \text{ m}^{-3})} \\
 &= \mathbf{7.0472 \times 10^{-8} \text{ m}}
 \end{aligned}$$

SOLVED PROBLEM 19. Calculate the critical temperature of a vander Waals gas for which P_c is 100 atm and b is $50 \text{ cm}^3 \text{ mol}^{-1}$.

SOLUTION :**(i) To calculate V_c** **Formula used**

$$V_c = 3b$$

Quantities given

$$b = 0.050 \text{ cm}^3 \text{ mol}^{-1} = 0.050 \text{ lit mol}^{-1}$$

Substitution of values

$$V_c = 3 \times 0.050 \text{ lit mol}^{-1} \\ = \mathbf{0.150 \text{ lit mol}^{-1}}$$

(ii) To calculate T_c

Formula used

$$T_c = \frac{8 P_c V_c}{3 R}$$

Quantities given

$$P_c = 100 \text{ atm}$$

$$V_c = 0.150 \text{ lit mol}^{-1}$$

$$R = 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1}$$

Substitution of values

$$T_c = \frac{8 \times 100 \text{ atm} \times 0.150 \text{ lit mol}^{-1}}{3 \times 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1}} \\ = 487.2 \text{ K} \\ = 487.2 - 273 \text{ }^\circ\text{C} \\ = \mathbf{214.2 \text{ }^\circ\text{C}}$$

SOLVED PROBLEM 20. Calculate molar volume of an ideal gas at $127 \text{ }^\circ\text{C}$ and 1 atm pressure.

SOLUTION :

Formula used

$$P V = n R T \quad \text{or} \quad V = \frac{n R T}{P}$$

Quantities given

$$n = 1 \text{ mole}$$

$$R = 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1}$$

$$T = 127 + 273 = 400 \text{ K}$$

Substitution of values

$$V = \frac{1 \text{ mole} \times 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 400 \text{ K}}{1 \text{ atm}} \\ = \mathbf{32.84 \text{ lit}}$$

SOLVED PROBLEM 21. The average velocity at $T_1 \text{ K}$ and most probable velocity of CO_2 at $T_2 \text{ K}$ is $9 \times 10^4 \text{ cm sec}^{-1}$. Calculate the value of T_1 and T_2 .

SOLUTION :

(i) To calculate the value of T_1

Formula used

$$v = \sqrt{\frac{8 R T_1}{\pi M}} \quad \text{or} \quad T_1 = \frac{v^2 \times \pi \times M}{8 R}$$

Quantities given

$$v = 9 \times 10^4 \text{ cm sec}^{-1}$$

$$R = 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}$$

$$M = 44 \text{ g mol}^{-1}$$

Substitution of values

$$T_1 = \frac{(9 \times 10^4 \text{ cm sec}^{-1})^2 \times 3.14 \times 44 \text{ g mol}^{-1}}{8 \times 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}} \\ = \frac{81 \times 10^8 \times 3.14 \times 44}{8 \times 8.314 \times 10^7} \text{ K} = \mathbf{1682.5 \text{ K}}$$

(ii) To calculate the value of T_2 **Formula used**

$$\mu_{mp} = \sqrt{\frac{2RT_2}{M}} \quad \text{or} \quad T_2 = \frac{(\mu_{mp})^2 \times M}{2R}$$

Quantities given

$$\mu_{mp} = 9 \times 10^4 \text{ cm sec}^{-1} \quad R = 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1} \quad M = 44 \text{ g mol}^{-1}$$

Substitution of values

$$\begin{aligned} T_2 &= \frac{(9 \times 10^4 \text{ cm sec}^{-1})^2 \times 44 \text{ g mol}^{-1}}{2 \times 8.314 \times 10^7 \text{ erg K}^{-1} \text{ mol}^{-1}} \\ &= \frac{81 \times 10^8 \times 44}{2 \times 8.314 \times 10^7} \text{ K} \\ &= \mathbf{2143 \text{ K}} \end{aligned}$$

SOLVED PROBLEM 22. Calculate the volume occupied by 5 g of acetylene gas at 50 °C and 740 mm pressure.

SOLUTION :**Formula used**

$$PV = nRT \quad \text{or} \quad V = \frac{nRT}{P}$$

Quantities given

$$\begin{aligned} n &= \frac{5 \text{ g}}{26 \text{ g mol}^{-1}} = 0.1923 \text{ mol}^{-1} & R &= 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \\ T &= 50 + 273 = 323 \text{ K} & P &= 740 \text{ mm} = \frac{740 \text{ mm}}{760 \text{ mm}} \times 1 \text{ atm} = 0.9737 \text{ atm} \end{aligned}$$

Substitution of values

$$\begin{aligned} V &= \frac{0.1923 \text{ mol}^{-1} \times 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 323 \text{ K}}{0.9737 \text{ atm}} \\ &= \mathbf{5.2377 \text{ lit}} \end{aligned}$$

SOLVED PROBLEM 23. At 27 °C hydrogen is leaked through a tiny hole into a vessel for 20 minutes. Another unknown gas at the same temperature and pressure, as that of H_2 , is leaked through the same hole for 20 minutes. After the effusion of gases the mixture exerts a pressure of 6 atm. The hydrogen content of the mixture is 0.7 mole. If the volume of the container is 3 litres, what is the molecular mass of the unknown gas.

SOLUTION :**(i) To calculate to the total number of moles in the mixture****Formula used**

$$PV = nRT \quad \text{or} \quad n = \frac{PV}{RT}$$

Quantities given

$$\begin{aligned} P &= 6 \text{ atm} & V &= 3 \text{ lit} & T &= 27 + 273 = 300 \text{ K} \\ R &= 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \end{aligned}$$

Substitution of values

$$\begin{aligned} n &= \frac{6 \text{ atm} \times 3 \text{ lit}}{0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}} \\ &= \mathbf{0.7308 \text{ mol}} \end{aligned}$$

$$\begin{aligned}
 \text{Number of moles of unknown gas} &= \text{Total number of moles} - \text{moles of hydrogen} \\
 &= 0.7308 - 0.7 \text{ mol} \\
 &= 0.0308 \text{ mol}
 \end{aligned}$$

(ii) To calculate the molecular mass of the unknown gas**Formula used**

$$\frac{r_{H_2}}{r_{gas}} = \sqrt{\frac{M_{gas}}{M_{H_2}}}$$

Quantities given

$$\begin{aligned}
 \frac{r_{H_2}}{r_{gas}} &= \frac{\text{amt of } H_2}{\text{amt of gas}} = \frac{0.7 \text{ mol}}{0.0308 \text{ mol}} \\
 M_{H_2} &= 2 \text{ g mol}^{-1}
 \end{aligned}$$

Substitution of values

$$\frac{0.7}{0.0308} = \sqrt{\frac{M_{gas}}{2}}$$

Squaring both sides

$$\frac{0.7 \times 0.7}{0.0308 \times 0.0308} = \frac{M_{gas}}{2 \text{ g mol}^{-1}}$$

or

$$M_{gas} = 1033 \text{ g mol}^{-1}$$

SOLVED PROBLEM 24. A gas bulb of 1 litre capacity contains 2.0×10^{21} molecules of nitrogen exerting a pressure of $7.57 \times 10^3 \text{ Nm}^2$. Calculate the RMS velocity and the temperature of the gas molecules. If the ratio of most probable velocity to RMS velocity is 0.82, calculate the most probable velocity for these molecules at this temperature.

SOLUTION :**(i) To calculate the RMS velocity of N_2 molecules****Formula used**

$$\mu = \sqrt{\frac{3P}{D}}$$

Quantities given

$$\begin{aligned}
 P &= 7.57 \times 10^3 \text{ Nm}^{-2} \\
 D &= \frac{\text{Mass}}{\text{Volume}} = \frac{28 \text{ g} \times 2 \times 10^{21} \text{ molecules}}{1 \text{ lit} \times 6.023 \times 10^{23} \text{ mol}^{-1}} \\
 &= 0.0929 \text{ g lit}^{-1} \\
 &= \frac{0.0929 \times 10^{-3}}{10^{-3}} \text{ kg m}^{-3} \\
 &= 0.0929 \text{ kg m}^{-3}
 \end{aligned}$$

Substitution of values

$$\begin{aligned}
 \mu &= \sqrt{\frac{3 \times 7.57 \times 10^3 \text{ Nm}^{-2}}{0.0929 \text{ kg m}^{-3}}} \\
 &= \sqrt{244456.40} \\
 &= 494.425 \text{ m sec}^{-1}
 \end{aligned}$$

(ii) To calculate the temperature of the gas

Formula used

$$\mu = \sqrt{\frac{3RT}{M}} \quad \text{or} \quad T = \frac{M\mu^2}{3R}$$

Quantities given

$$M = 28 \times 10^{-3} \text{ kg mol}^{-1}$$

$$\mu = 494.425 \text{ m sec}^{-1}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

Substitution of values

$$\begin{aligned} T &= \frac{(28 \times 10^{-3} \text{ kg mol}^{-1}) \times (494.425 \text{ m sec}^{-1})^2}{3 \times (8.314 \text{ J K}^{-1} \text{ mol}^{-1})} \\ &= \mathbf{274.43 \text{ K}} \end{aligned}$$

(ii) To calculate most probable velocity

$$\frac{\text{Most probable velocity, } \mu_{mp}}{\text{Root Mean Square Velocity, } \mu} = 0.82 \text{ (given)}$$

 \therefore

$$\begin{aligned} \text{Most probable velocity, } \mu_{mp} &= \text{RMS velocity} \times 0.82 \\ &= 494.425 \text{ m sec}^{-1} \times 0.82 \\ &= \mathbf{405.43 \text{ m sec}^{-1}} \end{aligned}$$

SOLVED PROBLEM 25. A balloon of diameter 20 m. weighs 100 kg. Calculate its pay-load if it is filled with Helium at 1 atm and 27 °C. Density of air 1.2 kg m⁻³ ($R = 0.082 \text{ atm dm}^3 \text{ K}^{-1}$)

SOLUTION :**(i) To calculate the mass of Helium gas present in the balloon**

Formula used

$$PV = nRT \quad \text{or} \quad n = \frac{PV}{RT}$$

Quantities given

$$P = 1 \text{ atm} \quad V = \frac{4}{3}\pi r^3 = \frac{4}{3} \times 3.14 \times (10\text{m})^3 = 4186.66 \text{ m}^3 = 4186.66 \times 10^3 \text{ dm}^3$$

$$R = 0.082 \text{ atm K}^{-1} \text{ mol}^{-1} \text{ dm}^3$$

$$T = 27 + 273 = 300 \text{ K}$$

Substitution of values

$$n = \frac{1 \text{ atm} \times 4186.66 \times 10^3 \text{ dm}^3}{0.082 \text{ atm dm}^3 \text{ K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}$$

$$= 170.189 \times 10^3 \text{ mol}$$

$$\text{Mass of Helium present} = 4 \text{ g mol}^{-1} \times 170.189 \times 10^3 \text{ mol}$$

$$= 680.76 \times 10^3 \text{ g}$$

$$= 680.76 \text{ kg}$$

$$\therefore \text{Mass of the filled balloon} = \text{Mass of the balloon} + \text{Mass of Helium present}$$

$$= 100 \text{ kg} + 680.76 \text{ kg}$$

$$= 780.76 \text{ kg}$$

(ii) To calculate the pay load

$$\text{Mass of the displaced air} = \text{Volume} \times \text{density}$$

$$= 4186.66 \text{ m}^3 \times 1.2 \text{ kg m}^{-3}$$

$$= 5023.99 \text{ kg}$$

 \therefore

$$\text{Pay load} = \text{Mass of displaced air} - \text{Total mass of balloon}$$

$$\begin{aligned}
 &= 5023.99 \text{ kg} - 780.76 \text{ kg} \\
 &= \mathbf{4243.23 \text{ kg}}
 \end{aligned}$$

SOLVED PROBLEM 26. An LPG (liquified petroleum gas) cylinder weighs 14.8 kg when empty. When full it weighs 29.0 kg and shows a pressure of 2.5 atm. In the course of use at 27 °C the weight of the full cylinder reduces to 23.2 kg. Find out the volume of the gas in cubic meters used up at the normal usage conditions and the final pressure inside the gas. Assume LPG to be *n*-butane with normal boiling of 0 °C.

SOLUTION :

(i) To calculate the volume of the gas initially present

$$\begin{aligned}
 \text{Mol mass of LPG (} n\text{-C}_4\text{H}_{10}\text{)} &= 12 \times 4 + 10 \times 1 = 58.0 \text{ g mol}^{-1} = 58 \times 10^{-3} \text{ kg mol}^{-1} \\
 \text{Weight of the full cylinder} &= 29.0 \text{ kg} \\
 \text{Weight of the empty cylinder} &= 14.8 \text{ kg} \\
 \text{Weight of gas initially present} &= 29.0 \text{ kg} - 14.8 \text{ kg} = 14.2 \text{ kg} \\
 \text{No. of moles of } n\text{-butane initially present} &= \frac{14.2 \text{ kg}}{58 \times 10^{-3} \text{ kg mol}^{-1}} \\
 &= 244.827 \text{ mol} \\
 \text{Pressure of the gas before use} &= 2.5 \text{ atm} \\
 \text{Initial volume of the gas, } V &= \frac{nRT}{P} = \frac{244.827 \text{ mol} \times 0.0821 \text{ atm lit}^{-1} \text{ K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{2.5 \text{ atm}} \\
 &= \mathbf{2214.97 \text{ lit}}
 \end{aligned}$$

(ii) To calculate the pressure of the gas after use

$$\begin{aligned}
 \text{Weight of cylinder after} &= 23.2 \text{ kg} \\
 \text{Weight of empty cylinder} &= 14.8 \text{ kg} \\
 \therefore \text{Weight of the gas unused gas} &= 23.2 \text{ kg} - 14.8 \text{ kg} \\
 &= 8.4 \text{ kg} \\
 \text{Pressure of gas after use } P &= \frac{nRT}{V} \\
 &= \frac{8.4 \text{ kg}}{58 \times 10^{-3} \text{ kg mol}^{-1}} \times \frac{0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{2214.97 \text{ lit}} \\
 &= \mathbf{1.4788 \text{ atm}}
 \end{aligned}$$

(iii) To calculate the volume of the gas after used

$$\begin{aligned}
 \text{Weight of the gas initially present} &= 14.2 \text{ kg} \\
 \text{Weight of gas after use} &= 8.4 \text{ kg} \\
 \text{Weight of the gas used up} &= 14.2 \text{ kg} - 8.4 \text{ kg} \\
 &= 5.8 \text{ kg} \\
 \text{Pressure under normal conditions of usage} &= 1 \text{ atm} \\
 \therefore \text{Volume of the gas used up, } V &= \frac{nRT}{P} \\
 &= \frac{5.8 \text{ kg} \times 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{58 \times 10^{-3} \text{ kg mol}^{-1} \times 1 \text{ atm}} \\
 &= 2463 \text{ lit} \\
 &= \mathbf{2.463 \text{ m}^3}
 \end{aligned}$$

SOLVED PROBLEM 27. A 4 : 1 mixture of Helium and methane is contained in vessel at 20 bar pressure. Due to a hole in the vessel, the gas mixture leaks out. What is the composition of the mixture effusing out initially.

SOLUTION :**(i) To calculate the partial pressure of He and CH₄**

$$\text{Ratio of moles He and CH}_4 = 4 : 1 \quad (\text{given})$$

$$\text{Total no. of moles} = 5$$

Pressure \propto no. of moles of the gas at constant V and T

$$\begin{aligned} \therefore \text{Partial pressure of He, } P_{He} &= \frac{\text{No. of moles of He}}{\text{Total no. of moles}} \times \text{Total pressure} \\ &= \frac{4}{5} \times (20 \text{ bar}) \\ &= 16 \text{ bar} \end{aligned}$$

$$\begin{aligned} \text{and Partial pressure of CH}_4, P_{CH_4} &= \frac{\text{No. of moles of CH}_4}{\text{Total no. of moles}} \times \text{Total pressure} \\ &= \frac{1}{5} \times (20 \text{ bar}) \\ &= 4 \text{ bar} \end{aligned}$$

(ii) To calculate the rates of effusion of He and CH₄

$$\text{Rate of effusion of Helium, } r_{He} = \frac{k \times P_{He}}{\sqrt{M_{He}}}$$

$$\text{Mol. mass of He, } M_{He} = 4$$

$$\begin{aligned} \therefore r_{He} &= \frac{k \times 16 \text{ bar}}{\sqrt{4}} \\ &= 8k \end{aligned}$$

$$\text{and Rate of effusion of CH}_4, r_{CH_4} = \frac{k \times P_{CH_4}}{\sqrt{M_{CH_4}}}$$

$$\text{Mol. mass of CH}_4, M_{CH_4} = 16$$

$$\begin{aligned} \therefore r_{CH_4} &= \frac{k \times (4 \text{ bar})}{\sqrt{M_{CH_4}}} \\ &= k \end{aligned}$$

Hence the rate of gases effusing out initially is $8k : k$ or $8 : 1$

SOLVED PROBLEM 28. An iron cylinder contains helium at a pressure of 250 k Pa at 300K. The cylinder can withstand a pressure of 1×10^6 Pa. The room in which cylinder is placed catches fire. Predict whether the cylinder will blow up before it melts or not. (melting point of cylinder = 1800 K)

SOLUTION :**To calculate the final pressure**

Formula used

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \text{or} \quad P_2 = \frac{P_1 V_1 T_2}{T_1 V_2}$$

Quantities given

Initial conditions : $P_1 = 250 \text{ k Pa} = 250 \times 10^3 \text{ Pa}$

$T_1 = 300 \text{ K}$

$V_1 = V \text{ lit}$

Final conditions : $V_2 = V \text{ lit}$

$T_2 = 1800 \text{ K}$

[\because volume remains the same]

Substitution of values

$$\begin{aligned} P_2 &= \frac{250 \times 10^3 \text{ Pa} \times 1800 \text{ K} \times V \text{ lit}}{300 \text{ K} \times V \text{ lit}} \\ &= 1500 \times 10^3 \text{ Pa} \\ &= \mathbf{1.5 \times 10^6 \text{ Pa}} \end{aligned}$$

Since the cylinder can withstand a pressure of $1 \times 10^6 \text{ Pa}$, it will definitely blow up at the melting point of cylinder as the pressure becomes $1.5 \times 10^6 \text{ Pa}$ when the cylinder melts.

SOLVED PROBLEM 29. 20 dm^3 of SO_2 diffuse through a porous partition in 60 sec. What volume of O_2 will diffuse under similar conditions in 30 sec ?

SOLUTION :

Formula used

$$\frac{r_{\text{SO}_2}}{r_{\text{O}_2}} = \sqrt{\frac{M_{\text{O}_2}}{M_{\text{SO}_2}}}$$

Quantities given

$$\begin{aligned} r_{\text{SO}_2} &= \frac{\text{Vol. of SO}_2}{\text{Time taken}} = \frac{20 \text{ dm}^3}{60 \text{ sec}} & M_{\text{SO}_2} &= 64 \text{ g mol}^{-1} \\ r_{\text{O}_2} &= \frac{\text{Vol. of O}_2}{\text{Time taken}} = \frac{V_{\text{O}_2} \text{ dm}^3}{30 \text{ sec}} & M_{\text{O}_2} &= 32 \text{ g mol}^{-1} \end{aligned}$$

Substitution of values

$$\begin{aligned} \frac{\frac{20 \text{ dm}^3}{60 \text{ sec}}}{\frac{V_{\text{O}_2} \text{ dm}^3}{30 \text{ sec}}} &= \sqrt{\frac{32 \text{ g mol}^{-1}}{64 \text{ g mol}^{-1}}} \\ \frac{10}{V_{\text{O}_2}} &= \sqrt{\frac{1}{2}} \\ \text{or } V_{\text{O}_2} &= 10 \times \sqrt{2} \text{ dm}^3 \\ &= 10 \times 1.414 \text{ dm}^3 \\ &= \mathbf{14.14 \text{ dm}^3} \end{aligned}$$

SOLVED PROBLEM 30. The molar volume of liquid benzene (density = 0.877 g ml^{-1}) increases by a factor of 2750 as it vapourises at 20°C and that of liquid toluene (density = 0.867 g ml^{-1}) increases by a factor of 7720 at 20°C . A solution of benzene and toluene at 20°C has vapour of 46.0 torr. Find the mole fraction of benzene in the vapour above the solution.

SOLUTION :

Formula used

$$p^o = \frac{nRT}{V}$$

Quantities given for benzene

$$n = 1 \text{ mole}$$

$$R = 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1}$$

$$T = 20 + 273 = 293 \text{ K}$$

$$\begin{aligned}\text{Volume of 1 mole of liquid benzene} &= \frac{M}{D} = \frac{78 \text{ g}}{0.877 \text{ g ml}^{-1}} \\ &= 88.939 \text{ ml}\end{aligned}$$

$$\begin{aligned}\text{and Volume of 1 mole of benzene vapours} &= 2750 \times 88.939 \text{ ml} \\ &= 244582 \text{ ml} \\ &= 244.582 \text{ lit}\end{aligned}$$

Substitution of values

$$\begin{aligned}p_{\text{benzene}}^{\circ} &= \frac{1 \text{ mole} \times 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 293 \text{ K}}{244.582 \text{ lit}} \\ &= 0.098 \text{ atm}\end{aligned}$$

Quantities given for toluene

$$n = 1 \text{ mole} \quad R = 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \quad T = 293 \text{ K}$$

$$\begin{aligned}\text{Volume of 1 mole of liquid toluene} &= \frac{M}{D} = \frac{92 \text{ g}}{0.867 \text{ g ml}^{-1}} \\ &= 106.11 \text{ ml}\end{aligned}$$

$$\begin{aligned}\text{and Volume of 1 mole toluene vapours} &= 7720 \times 106.11 \text{ ml} \\ &= 819169 \text{ ml} \\ &= 819.169 \text{ lit}\end{aligned}$$

Substitution of values

$$\begin{aligned}p_{\text{toluene}}^{\circ} &= \frac{1 \text{ mole} \times 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 293 \text{ K}}{819.169 \text{ lit}} \\ &= 0.029 \text{ atm}\end{aligned}$$

(ii) To calculate the mole fraction of benzene**Formula used**

$$x_{\text{benzene}} \times p_{\text{benzene}}^{\circ} + x_{\text{toluene}} \times p_{\text{toluene}}^{\circ} = \text{Total pressure}$$

Quantities given

$$\text{Total pressure} = 46 \text{ torr} = \frac{46 \text{ torr}}{760 \text{ torr}} = 0.06 \text{ atm}$$

$$p_{\text{benzene}}^{\circ} = 0.098 \quad p_{\text{toluene}}^{\circ} = 0.029 \text{ atm} \quad x_{\text{toluene}} = 1 - x_{\text{benzene}}$$

Substitution of values

$$x_{\text{benzene}} \times 0.098 \text{ atm} + (1 - x_{\text{benzene}}) 0.029 \text{ atm} = 0.06 \text{ atm}$$

$$\begin{aligned}\text{or } x_{\text{benzene}} &= \frac{0.06 - 0.029}{(0.098 - 0.029)} \\ &= \mathbf{0.449}\end{aligned}$$

ADDITIONAL PRACTICE PROBLEMS

1. A 5.0 litre sample of gas has its pressure doubled while its absolute temperature is increased by 25%. What is its new volume ?
Answer. 3.125 lit
2. The total pressure of a mixture of gases is 1.50 atm. The mixture contains 0.1 mole of N_2 and 0.2 mole of O_2 . What is the partial pressure of O_2 ?

Answer. 1.0 atm

3. Calculate the RMS, average and most probable velocity of a gas at 25 °C, when the mass of a gas molecule is 4.468×10^{-26} g.

Answer. 5.274×10^4 cm sec⁻¹ ; 4.859×10^4 cm sec⁻¹ ; 4.306×10^4 cm sec⁻¹

4. Calculate the RMS velocity of CO₂ at 27 °C.

Answer. 4.1328×10^4 cm sec⁻¹

5. Calculate the mean free path for O₂ molecule at 300 K and pressure 101.325 kPa. The collision diameter of oxygen molecule is 0.326 nm.

Answer. 7.0169×10^{-8} m

6. Calculate the pressure developed in 95 litre vessel containing 88 g of CO₂ at 27°C. Assume CO₂ is vander Waals gas ($C = 12$; $O = 16$ $a = 3.59$ atm lit² mol⁻² ; $b = 0.043$ lit mol⁻¹)

Answer. 9.450 atm

7. Calculate the critical temperature of a vander Waals gas for which P_c is 100 atm and b is 50 cm³ mol⁻¹.

Answer. 214.2 °C

8. The pressure in a bulb dropped from 2000 to 150 mm of Hg in 47 minutes when the contained oxygen leaked through a small hole. The bulb was then evacuated. A mixture of oxygen and another gas with molar ratio 1:1 at a pressure of 4000 mm Hg was introduced. Find the molar ratio of two gas remaining in the bulb after 74 minutes.

Answer. 4 : 5

9. Calculate the average kinetic energy in Joules of the molecules in 8.0 g of methane at 27 °C.

Answer. 1870.65 J

10. At room temperature ammonia gas at 1 atm pressure and hydrogen chloride at P atm pressure are allowed to effuse through identical pin holes from opposite ends of a glass tube of one meter length and of uniform cross-section. Ammonium Chloride is first formed at 60 cm from the end through which hydrogen chloride is sent in. What is the value of P ?

Answer. 2.197 atm

11. When 2 g of a gas is introduced into an evacuated flask kept at 25 °C, the pressure is found to be 1 atm. If 3 g of another gas B is then added to same flask the total pressure becomes 1.5 atm. Assuming ideal behaviour, calculate the ratio of their molecular mass $M_A : M_B$.

Answer. 1.3

12. Oxygen is present in 1 litre flask at a pressure of 7.6×10^{-10} mm of Hg. Calculate the number of oxygen molecules in the flask at 0 °C.

Answer. 3.224×10^{11} molecules

13. Calculate the root mean square velocity of Ozone kept in a closed vessel at 20 °C and 82 cm mercury pressure.

Answer. 3.9032×10^4 cm sec⁻¹

14. A spherical balloon of 21 cm diameter is to be filled up with hydrogen at NTP from a cylinder containing the gas at 27 °C and 27 atm pressure. If the cylinder can hold 2.82 litre of water, calculate the number of balloons that can be filled up.

Answer. 10

15. At 27 °C, hydrogen is leaked through a tiny hole into a vessel for 22 minutes. Another unknown gas at the same temperature and pressure as that of H₂ is leaked through the same hole for 20 minutes. After the effusion of the gases, the mixture exerts a pressure of one atmosphere. The hydrogen content of the mixture is 0.7 mole. If the volume of container is 3.0 litre, what is the molecular mass of the unknown gas.

Answer. 1020 g mol⁻¹

16. The composition of the equilibrium mixture ($\text{Cl}_2 = 2 \text{ Cl}$), which is attained at 1200°C , is determined by measuring the rate of effusion through a pin-hole. It is observed that at 1.80 mm Hg pressure, the mixture effuses 1.16 times as fast as Krypton effuses under the same conditions. Calculate the fraction of chlorine molecules dissociated into atoms (Atomic weight of Kr = 84).
Answer. 0.137
17. What weight of AgCl would be precipitated if 10 ml of HCl gas, measured at 12°C and 750 mm pressure were passed into excess of a solution of silver nitrate?
Answer. 0.606 g
18. Calculate the total pressure in a mixture of 4 g of oxygen and 3 g of hydrogen confined in a total volume of one litre at 0°C .
Answer. 25.18 atm
19. Calculate the volume occupied by 7 g of nitrogen gas at 27°C and 750 mm pressure.
Answer. 6.23 litre
20. Two gases P and Q having molecular masses 44 and 64 respectively are enclosed in a vessel. Their masses are 0.5 g and 0.3 g respectively and the total pressure of the mixture is 740 mm. Calculate the partial pressures of the two gases.
Answer. 524 mm ; 216 mm
21. Calculate the total pressure in a 10 Litre cylinder which contains 0.4 g of helium, 1.6 g of oxygen and 1.4 of nitrogen at 27°C . Also calculate the partial pressure of helium gas in the cylinder. Assume ideal behaviour for gases.
Answer. 0.492 atm ; 0.246 atm

11

The Liquids

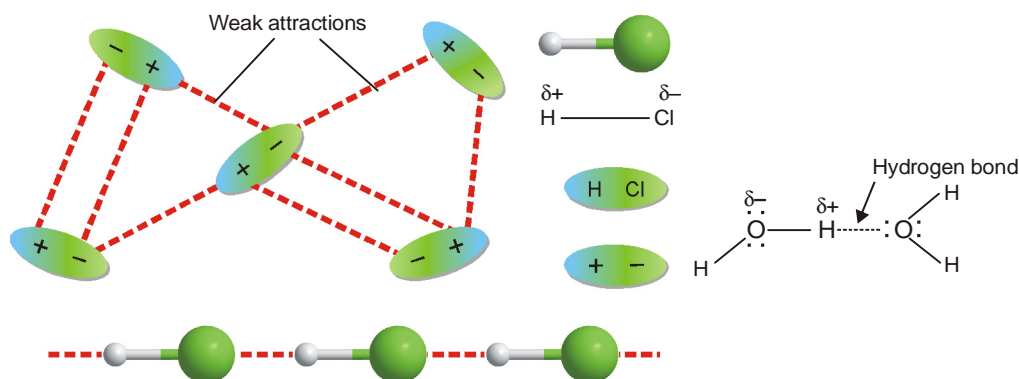
CHAPTER

KEY CONCEPTS AND EQUATIONS



INTERMOLECULAR FORCES IN LIQUIDS

In the liquid state the molecules are in contact with each other. The forces of attraction between the molecules are strong enough to hold them together. The forces of attraction between the molecules are collectively called **van der Waals'** forces. These are weak attractive forces in large number of substances like HCl, Cl_2 , Br_2 , etc. The strength of van der Waals' forces range from 0.1 to 10 kJ mol^{-1} . Hydrogen bonding occurs in substances having hydrogen covalently bonded to a highly electronegative atom.



■ **Figure 11.1**
van der Waal's forces and hydrogen bonding.

The strength of hydrogen bond is of the order of 10 to 40 kJ mol^{-1} . It is about one-tenth as strong as covalent bond.

VAPOUR PRESSURE

The vapour pressure of a liquid is the partial pressure of the vapour over the liquid at equilibrium. The vapour pressure of different liquids depend upon their nature and the intermolecular forces. For example, ethyl alcohol has weaker hydrogen bonding than water and evaporates faster than water. With rise in temperature the vapour pressure increases.

BOILING POINT

When the vapour pressure becomes equal to the atmospheric pressure boiling occurs. **The temperature at which the vapour pressure of a liquid becomes equal to the atmospheric pressure is called the boiling point.** The graph between the vapour pressure and temperature for some liquids is shown in Fig.1.2 which shows that vapour pressure increases rapidly with temperature.

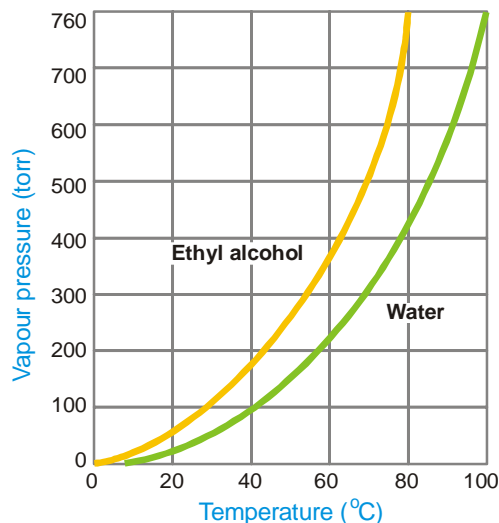


Figure 11.2
Variation of vapour pressure with temperature.

SURFACE TENSION

It is defined as the energy required to increase the surface area of a liquid by a unit amount. It is measured by dynes cm^{-1} (CGS unit) or in Newton per meter, Nm^{-1} (SI units) or Jm^{-2} .

DETERMINATION OF SURFACE TENSION

(i) Capillary rise method

The formula used for the determination of surface tension by capillary rise method is

$$\gamma = \frac{h r d g}{2}$$

where h is the height to which liquid rises in a capillary tube of radius r ; d is density of the liquid and g the force of gravity.

(ii) Drop-weight method

The formula used in drop weight method is

$$\frac{\gamma_1}{\gamma_2} = \frac{m_1}{m_2}$$

where γ_1 and γ_2 are the surface tension of given liquid and water, m_1 and m_2 the masses of one drop of each liquid and water respectively. Knowing the surface tension of reference liquid γ_2 , the surface tension of the liquid under study can be calculated.

(iii) Drop-number method

The formula used is

$$\frac{\gamma_1}{\gamma_2} = \frac{n_2}{n_1} \times \frac{d_1}{d_2}$$

where γ_1 and γ_2 are the surface tension of given liquid and water respectively, n_1 & n_2 are the number of drops in a given volume, d_1 and d_2 are their densities.

VISCOSITY

Viscosity is the resistance to flow that is exhibited by all liquids. It may be defined as the force of resistance per unit area which will maintain unit velocity difference between two layers of a liquid at a unit distance from each other. It is denoted by η . Its units are mass $\text{length}^{-1} \text{time}^{-1}$ i.e. $\text{kg m}^{-1} \text{sec}^{-1}$ (SI units) or $\text{g cm}^{-1} \text{sec}^{-1}$ (CGS units) and

$$1 \text{ poise} = 1 \text{ g cm}^{-1} \text{sec}^{-1} = 0.1 \text{ kg m}^{-1} \text{sec}^{-1}$$

DETERMINATION OF VISCOSITY**Ostwald's method**

The formula used for the determination of viscosity by the Ostwald's method is

$$\eta = \frac{\pi P r^4 t}{8 l V}$$

where V is the volume of the liquid flowing through a capillary in time t , P is the pressure-head, r , the radius of the tube and l its length.

The relative viscosity is given by the relation

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2}$$

where t_1 and t_2 are times of flow of fixed volume (V) of two liquids with densities d_1 and d_2 respectively.

Knowing the value of η_2 , η_1 can be calculated.

REFRACTIVE INDEX

The refractive index n of a substance is defined as the ratio of velocity of light in substance to that in air or vacuum.

$$n = \frac{\text{Velocity of light in substance}}{\text{Velocity of light in air}}$$

The refractive index of the liquid with respect to air is given by Snelle's law

$$n = \frac{\sin i}{\sin r}$$

where i is the angle of incidence and r , the angle of refraction.

SPECIFIC REFRACTION

It is given by the formula

$$R_s = \frac{n^2 - 1}{n^2 + 2} \times \frac{1}{d}$$

where R_s is the specific refraction, d the density and n is the refractive index

MOLAR REFRACTION

It is the product of specific refraction and molecular mass

i.e.

$$R_M = \frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d}$$

where M is the molecular mass of the substance.

OPTICAL ACTIVITY

A compound that can rotate the plane of polarised light is called optically active. This property of a compound is called optical activity.

SPECIFIC ROTATION

It is expressed as

$$[\alpha] = \frac{\alpha}{l \times c}$$

where $[\alpha]$ is the specific rotation in degrees
 α , the observed angle of rotation in degrees
 l , the length of the sample in decimeter
 C , the concentration of the sample solution in g cm^{-3} .

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. A capillary tube of internal diameter 0.2 mm is dipped into water when water rises 15 cm. Calculate the surface tension of water.

SOLUTION :**Formula used**

$$\gamma = \frac{(h + \frac{1}{3} r) r \rho g}{2}$$

Quantities given

$$r = 0.1 \text{ mm} = 0.01 \text{ cm}$$

$$h = 15 \text{ cm}$$

$$\rho = 1 \text{ g cm}^{-3}$$

$$g = 980 \text{ cm sec}^{-2}$$

Substitution of values

$$\begin{aligned} \gamma &= \frac{(15 + \frac{1}{3} \times 0.01) \text{ cm} \times 0.01 \text{ cm} \times 980 \text{ cm sec}^{-2} \times 1 \text{ g cm}^{-3}}{2} \\ &= \mathbf{73.51 \text{ dyne cm}^{-1}} \end{aligned}$$

SOLVED PROBLEM 2. In a measurement of viscosity by Ostwald's viscometer at 20.2 °C, water takes 30 seconds to flow between the upper and lower marks while the flow of another liquid of density 1.5 g cm^{-3} takes 35 seconds. Taking density of water at 20.2 °C to be 0.9982 g cm^{-3} , calculate the viscosity of the other liquid if the viscosity of water at this temperature is 10 centipoise.

SOLUTION :**Formula used**

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2}$$

or

$$\eta_2 = \frac{\eta_1 d_2 t_2}{d_1 t_1}$$

Quantities given

$$\eta_1 = 10 \text{ centipoise}$$

$$d_1 = 0.9982 \text{ g cm}^{-3}$$

$$t_1 = 30 \text{ sec}$$

$$d_2 = 1.5 \text{ g cm}^{-3}$$

$$t_2 = 35 \text{ sec}$$

Substitution of values

$$\begin{aligned} \eta_2 &= \frac{10 \text{ centipoise} \times 1.5 \text{ g cm}^{-3} \times 35 \text{ sec}}{0.9982 \text{ g cm}^{-3} \times 30 \text{ sec}} \\ &= 17.53 \text{ centipoise} \\ &= \mathbf{0.1753 \text{ poise}} \end{aligned}$$

SOLVED PROBLEM 3. At 20 °C, toluene rises 1.95 cm in a capillary tube of radius 0.3412 mm. Calculate the surface tension of toluene. The density of toluene at 20 °C is 0.866 g cm^{-3} .

SOLUTION :**Formula used**

$$\gamma = \frac{(h + \frac{1}{3} r) r \rho g}{2}$$

Quantities given

$$h = 1.95 \text{ cm} \quad r = 0.3412 \text{ mm} = 0.03412 \text{ cm} \quad \rho = 0.866 \text{ g cm}^{-3} \quad g = 981 \text{ cm sec}^{-2}$$

Substitution of values

$$\begin{aligned}
 \gamma &= \frac{(1.95 + \frac{1}{3} \times 0.03412) \text{ cm} \times 0.03412 \text{ cm} \times 0.866 \text{ g cm}^{-3} \times 981 \text{ cm sec}^{-2}}{2} \\
 &= \frac{1.961373 \times 0.03412 \times 0.866 \times 981}{2} \text{ dynes cm}^{-1} \\
 &= 28.42 \text{ dynes cm}^{-1}
 \end{aligned}$$

SOLVED PROBLEM 4. The density of a liquid at 25 °C is 1.2 g ml⁻¹. Its refractive index n_D^{25} is 1.552. Calculate its molar refractivity. (Molecular mass of liquid = 123)

SOLUTION :**Formula used**

$$R_M = \frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d}$$

Quantities given

$$n = 1.552$$

$$d = 1.203 \text{ g ml}^{-1}$$

$$M = 123$$

Substitution of values

$$\begin{aligned}
 R_M &= \frac{(1.552)^2 - 1}{(1.552)^2 + 2} \times \frac{123}{1.203} \\
 &= \frac{1.4087}{4.4087} \times \frac{123}{1.203} \\
 &= 32.66 \text{ cm mol}^{-1}
 \end{aligned}$$

SOLVED PROBLEM 5. In an Ostwald viscometer, the flow times for two liquids A and B are in the ratio 4:5. If the density of liquid B is twice as high as that of A, calculate the ratio of their viscosities.

SOLUTION :**Formula used**

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2}$$

Quantities given

$$\text{Density of liquid A, } d_1 = d_1$$

$$\text{time for liquid A} = 4 t \text{ sec}$$

$$\text{Density of liquid B, } d_2 = 2 \times d_1$$

$$\text{time for liquid B} = 5 t \text{ sec}$$

Substitution of values

$$\frac{\eta_1}{\eta_2} = \frac{d_1 \times 4 t}{2 d_1 \times 5 t} = \frac{2}{5}$$

or

$$\eta_1 : \eta_2 = 2 : 5$$

SOLVED PROBLEM 6. Time taken for the same volume of water and benzene to flow in viscometer at 20° C have been found to be 120 seconds and 88 seconds respectively. The density of benzene at this temperature is 0.879 g cm⁻³. If the absolute viscosity of water at 20 °C is 10.05×10^{-3} poise, calculate the specific viscosity of benzene at this temperature.

SOLUTION :**Formula used**

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2} \quad \text{or} \quad \eta_2 = \frac{\eta_1 d_2 t_2}{d_1 t_1}$$

Quantities given

$$\begin{array}{lll} \eta_1 = 10.05 \times 10^{-3} \text{ poise} & d_1 = 1.0 \text{ g cm}^{-3} & t_1 = 120 \text{ sec} \\ & d_2 = 0.879 \text{ g cm}^{-3} & t_2 = 88 \text{ sec} \end{array}$$

Substitution of values

$$\begin{aligned} \eta_2 &= \frac{10.05 \times 10^{-3} \text{ poise} \times 0.879 \text{ g cm}^{-3} \times 88 \text{ sec}}{1.0 \text{ g cm}^{-3} \times 120 \text{ sec}} \\ &= \mathbf{6.4782 \times 10^{-3} \text{ poise}} \end{aligned}$$

SOLVED PROBLEM 7. It takes 100 sec for water to flow through a capillary tube at fixed pressure.

How long will it take toluene to do so under similar conditions? Given that :

$$\begin{array}{ll} \text{density of water} = 0.998 \text{ g cm}^{-3} & \text{absolute viscosity of water} = 0.01 \text{ dyne sec cm}^2 \\ \text{density of toluene} = 0.866 \text{ g cm}^{-3} & \text{viscosity} = 0.006 \text{ dyne sec cm}^{-2}. \end{array}$$

SOLUTION :**Formula used**

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2} \quad \text{or} \quad t_2 = \frac{\eta_2 d_1 t_1}{\eta_1 d_2}$$

Quantities given

$$\begin{array}{lll} \eta_1 = 0.01 \text{ dyne sec cm}^{-2} & d_1 = 0.998 \text{ g cm}^{-3} & t_1 = 100 \text{ sec} \\ \eta_2 = 0.006 \text{ dyne sec cm}^{-2} & d_2 = 0.866 \text{ g cm}^{-3} & \end{array}$$

Substitution of values

$$\begin{aligned} t_2 &= \frac{0.006 \text{ dyne sec cm}^{-2} \times 0.998 \text{ g cm}^{-3} \times 100 \text{ sec}}{0.01 \text{ dyne sec cm}^{-2} \times 0.866 \text{ g cm}^{-3}} \\ &= \mathbf{69.15 \text{ sec}} \end{aligned}$$

SOLVED PROBLEM 8. At 20 °C, pure water required 102.2 sec to flow the capillary of an Ostwald viscometer while toluene at 20 °C required 68.9 sec. Calculate the relative viscosity of toluene. Densities of water and toluene are 0.998 and 0.866 g cm⁻³.**SOLUTION :****Formula used**

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2} \quad \text{or} \quad \eta_2 = \frac{\eta_1 d_2 t_2}{d_1 t_1}$$

Quantities given

$$\begin{array}{lll} \eta_1 = 1 \text{ poise} & d_1 = 0.998 \text{ g cm}^{-3} & t_1 = 102.2 \text{ sec} \\ & d_2 = 0.866 \text{ g cm}^{-3} & t_2 = 68.9 \text{ sec} \end{array}$$

Substitution of values

$$\begin{aligned} \eta_2 &= \frac{1 \text{ poise} \times 0.866 \text{ g cm}^{-3} \times 68.9 \text{ sec}}{0.998 \text{ g cm}^{-3} \times 102.2 \text{ sec}} \\ &= \mathbf{0.5850 \text{ poise}} \end{aligned}$$

SOLVED PROBLEM 9. The rise of water level in a capillary of radius 0.2 mm at 20 °C is 7.4 cm. Calculate the surface tension of water taking its density as 1 g cm⁻³ at 20 °C.

SOLUTION :

Formula used

$$\gamma = \frac{(h + \frac{1}{3}r)r\rho g}{2}$$

Quantities given

$$h = 7.4 \text{ cm} \quad r = 0.2 \text{ mm} = 0.02 \text{ cm} \quad \rho = 1 \text{ g cm}^{-3} \quad g = 980 \text{ dynes sec}^{-1}$$

Substitution of values

$$\begin{aligned} \gamma &= \frac{(7.4 \times \frac{1}{3} \times 0.02) \text{ cm} \times 0.02 \text{ cm} \times 980 \text{ dynes sec}^{-1}}{2} \\ &= 72.65 \text{ dynes cm}^{-1} \end{aligned}$$

SOLVED PROBLEM 10. At 20 °C flow times of water and another liquid in a viscometer are 2 min 24 sec and 1 min respectively. Take density of water = 1 g cm⁻³ ; density of liquid = 0.8 g cm⁻³ ; viscosity coefficient of water = 1 centipoise (all at 20 °C). Calculate the viscosity coefficient for the liquid at 20 °C.

SOLUTION :

Formula used

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2} \quad \text{or} \quad \eta_2 = \frac{\eta_1 d_2 t_2}{d_1 t_1}$$

Quantities given

$$\begin{aligned} d_1 &= 1 \text{ g cm}^{-3} & t_1 &= 144 \text{ sec} & \eta_1 &= 1 \text{ centipoise} \\ d_2 &= 0.8 \text{ g cm}^{-3} & t_2 &= 60 \text{ sec} \end{aligned}$$

Substitutions of values

$$\begin{aligned} \eta_2 &= \frac{1 \text{ centipoise} \times 0.8 \text{ g cm}^{-3} \times 60 \text{ sec}}{1.0 \text{ g cm}^{-3} \times 144 \text{ sec}} \\ &= 0.33 \text{ centipoise} \end{aligned}$$

SOLVED PROBLEM 11. How long a machine oil take to pass through a viscometer if water under the same conditions takes one minute ? Density of water = 1.0 × 10³ kg m⁻³ ; $\eta = 0.00101 \text{ Nm}^{-2} \text{ sec}$; Density of oil = 0.97 × 10³ kg m⁻³ ; $\eta = 0.060 \text{ Nm}^{-2} \text{ sec}$.

SOLUTION :

Formula used

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2} \quad \text{or} \quad t_2 = \frac{\eta_2 d_1 t_1}{\eta_1 d_2}$$

Quantities given

$$\begin{aligned} \eta_1 &= 0.00101 \text{ Nm}^{-2} \text{ sec} & d_1 &= 1 \times 10^3 \text{ kg m}^{-3} & t_1 &= 60 \text{ sec} \\ \eta_2 &= 0.060 \text{ Nm}^{-2} \text{ sec} & d_2 &= 0.97 \times 10^3 \text{ kg m}^{-3} \end{aligned}$$

Substitution of values

$$\begin{aligned} t_2 &= \frac{0.060 \text{ Nm}^{-2} \text{ sec} \times 1 \times 10^3 \text{ kg m}^{-3} \times 60 \text{ sec}}{0.00101 \text{ Nm}^{-2} \text{ sec} \times 0.97 \times 10^3 \text{ kg m}^{-3}} \\ &= 3674.59 \text{ sec} \end{aligned}$$

SOLVED PROBLEM 12. Some volume of benzene takes 46 sec to flow through an Ostwald viscometer while an equal volume of water takes 68 sec at the same temperature. Their respective densities are 0.800 g cm^{-3} and 0.998 g cm^{-3} . Coefficient of viscosity of water under the conditions is 1.008 centipoise. Calculate the coefficient of viscosity of benzene.

SOLUTION :**Formula used**

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2} \quad \text{or} \quad \eta_2 = \frac{\eta_1 d_2 t_2}{d_1 t_1}$$

Quantities given

$$\begin{array}{lll} \eta_1 = 1.008 \text{ centipoise} & d_1 = 0.998 \text{ g cm}^{-3} & t_1 = 68 \text{ sec} \\ & d_2 = 0.800 \text{ g cm}^{-3} & t_2 = 46 \text{ sec} \end{array}$$

Substitution of values

$$\begin{aligned} \eta_2 &= \frac{1.008 \text{ centipoise} \times 0.800 \text{ g cm}^{-3} \times 46 \text{ sec}}{0.998 \text{ g cm}^{-3} \times 68 \text{ sec}} \\ &= \mathbf{0.05466 \text{ centipoise}} \end{aligned}$$

SOLVED PROBLEM 13. When 12.0 cc of water is allowed to flow through a stalgamometer, 50.0 drops of water were obtained and when the same volume of liquid is allowed to flow, the number of drops formed was 35. If the density of the liquid is 1.2 g per cc and the surface tension of water is 72 dynes cm^{-1} , calculate the surface tension of the liquid.

SOLUTION :**Formula used**

$$\frac{\gamma_1}{\gamma_2} = \frac{n_2 d_1}{n_1 d_2} \quad \text{or} \quad \gamma_2 = \frac{\gamma_1 n_1 d_1}{n_2 d_2}$$

Quantities given

$$\begin{array}{lll} n_1 = 35 & d_1 = 1.0 \text{ g cm}^{-3} & \gamma_1 = 72 \text{ dynes cm}^{-1} \\ n_2 = 50 & d_2 = 1.2 \text{ g cm}^{-3} & \end{array}$$

Substitution of values

$$\begin{aligned} \gamma_2 &= \frac{72 \text{ dynes cm}^{-1} \times 50 \times 1.2 \text{ g cm}^{-3}}{35 \times 1.0 \text{ g cm}^{-3}} \\ &= \mathbf{123.428 \text{ dyne cm}^{-1}} \end{aligned}$$

SOLVED PROBLEM 14. In an experiment at 293 K, water rose in a capillary of diameter 0.078 cm to a height of 3.96 cm. Calculate the surface tension of water if the density of water at this temperature is 0.998 g cm^{-3} and $g = 980 \text{ cm sec}^{-2}$.

SOLUTION :**Formula used**

$$\gamma = \frac{h r d g}{2}$$

Quantities given

$$h = 3.96 \text{ cm} \quad r = \frac{0.078}{2} = 0.039 \text{ cm}$$

$$d = 0.998 \text{ g cm}^{-3} \quad g = 980 \text{ cm sec}^{-2}$$

Substitution of values

$$\gamma = \frac{0.039 \text{ cm} \times 3.96 \text{ cm} \times 0.998 \text{ g cm}^{-3} \times 980 \text{ cm sec}^{-2}}{2}$$

$$= \frac{151.048}{2} \text{ dynes cm}^{-1} \quad [\because 1 \text{ dyne} = 1 \text{ g cm sec}^{-2}]$$

$$= 75.524 \text{ dynes cm}^{-1}$$

SOLVED PROBLEM 15. Fifty drops of water weigh 3.75 g and that of a liquid 0.850 g. Calculate the surface tension of the liquid if the surface tension of water is $72.7 \text{ dynes cm}^{-1}$.

SOLUTION :**Formula used**

$$\frac{\gamma_1}{\gamma_2} = \frac{m_1}{m_2}$$

Quantities given

$$\gamma_1 = 72.7 \text{ dynes cm}^{-1} \quad m_1 = \frac{3.75}{50} \text{ g} \quad m_2 = \frac{0.850}{50} \text{ g}$$

Substitution of values

$$\frac{72.7 \text{ dynes cm}^{-1}}{\gamma_2} = \frac{3.75}{50} \times \frac{50}{0.850}$$

or

$$\gamma_2 = \frac{72.7 \times 0.850}{3.75} \text{ dynes cm}^{-1}$$

$$= 16.479 \text{ dynes cm}^{-1}$$

SOLVED PROBLEM 16. The number of drops of water counted in a stalgamometer at 298 K is 300 whereas the number of drops for ethyl alcohol is 320. Calculate the surface tension of ethyl alcohol given that the density of water = 0.998 g cm^{-3} , density of ethyl alcohol = 0.9614 g cm^{-3} surface tension of water = $72.75 \text{ dynes cm}^{-1}$.

SOLUTION :**Formula used**

$$\frac{\gamma_1}{\gamma_2} = \frac{n_1}{n_2} \times \frac{d_1}{d_2}$$

Quantities given

$$\gamma_1 = 72.75 \text{ dynes cm}^{-1} \quad n_1 = 300 \quad d_1 = 0.998 \text{ g cm}^{-3}$$

$$n_2 = 320 \quad d_2 = 0.9614 \text{ g cm}^{-3}$$

Substitution of values

$$\frac{72.75 \text{ dynes cm}^{-1}}{\gamma_2} = \frac{300 \times 0.998 \text{ g cm}^{-3}}{320 \times 0.9614 \text{ g cm}^{-3}}$$

or

$$\gamma_2 = \frac{72.75 \times 320}{300} \times \frac{0.9614}{0.998}$$

$$= 77.75 \text{ dynes cm}^{-1}$$

SOLVED PROBLEM 17. The times of flow for the same volume of water and carbon tetrachloride, through an Ostwald's viscometer are 400 and 300 secs respectively. The densities of water and carbon tetrachloride are 0.998 and 1.542 g cm⁻³ respectively. Calculate the viscosity coefficient of carbon tetrachloride if the value for water is 0.01002 poise.

SOLUTION :**Formula used**

$$\frac{\eta_1}{\eta_2} = \frac{t_1}{t_2} \times \frac{d_1}{d_2}$$

Quantities given

$$\eta_1 = 0.01002 \text{ P}$$

$$t_1 = 400 \text{ sec}$$

$$d_1 = 0.998 \text{ g cm}^{-3}$$

$$t_2 = 300 \text{ sec}$$

$$d_2 = 1.542 \text{ g cm}^{-3}$$

Substitution of values

$$\frac{0.01002 \text{ P}}{\eta_2} = \frac{400 \text{ sec} \times 0.998 \text{ g cm}^{-3}}{300 \text{ sec} \times 1.542 \text{ g cm}^{-3}}$$

$$\text{or} \quad = \frac{0.01002 \times 300 \times 1.542}{400 \times 0.998} \text{ poise}$$

$$= \mathbf{0.01161 \text{ poise}}$$

SOLVED PROBLEM 18. In a measurement of viscosity with Ostwald's viscometer, water takes 580 sec to flow through a given volume, while an organic liquid takes 395 sec. Calculate the viscosity of organic liquid. Density of organic liquid and water are 0.7807 and 0.9984 g cm⁻³ respectively. Viscosity of water is 1.01 centipoise.

SOLUTION :**Formula used**

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2}$$

Quantities given

$$\eta_1 = 1.01 \text{ centipoise}$$

$$d_1 = 0.9984 \text{ g cm}^{-3}$$

$$t_1 = 580 \text{ sec}$$

$$d_2 = 0.7867 \text{ g cm}^{-3}$$

$$t_2 = 395 \text{ sec}$$

Substitution of values

$$\frac{1.01 \text{ centipoise}}{\eta_2} = \frac{0.9984 \text{ g cm}^{-3} \times 580 \text{ sec}}{0.7867 \text{ g cm}^{-3} \times 395 \text{ sec}}$$

$$\text{or} \quad \eta_2 = \frac{1.01 \times 0.7867 \times 395}{0.9984 \times 580} \text{ centipoise}$$

$$= \mathbf{0.542 \text{ centipoise}}$$

SOLVED PROBLEM 19. The refractive index of carbon tetrachloride is 1.4573 and its density is 1.5952 g cm⁻³. Calculate its molar refraction.

SOLUTION :**Formula used**

$$R_m = \frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d}$$

Quantities given

$$n = 1.4573$$

$$d = 1.5952 \text{ g cm}^{-3}$$

$$M = 12 + 4 \times 35.5 = 154 \text{ g mol}^{-1}$$

Substitution of values

$$\begin{aligned}
 R_m &= \frac{(1.4573)^2 - 1}{(1.4573)^2 + 2} \times \frac{154}{1.5952} \\
 &= \frac{1.1237}{4.1237} \times \frac{154}{1.5952} \\
 &= 26.30 \text{ cm}^3 \text{ mol}^{-1}
 \end{aligned}$$

SOLVED PROBLEM 20. A solution of a certain optically active substance in water containing 5.2 g in 30 ml is introduced in a 20 cm long polarimeter tube. It rotated plane polarised light by 6.2° . Calculate the specific rotation.

SOLUTION :**Formula used**

$$[\alpha] = \frac{\alpha}{l \times c}$$

Quantities given

$$\alpha = 6.2^\circ$$

$$l = 20 \text{ cm} = 2 \text{ dm}$$

$$c = \frac{5.2}{30} \text{ g ml}^{-1}$$

$$[\alpha] = \frac{6.2^\circ \times 30}{2 \times 5.2} = 17.88^\circ$$

ADDITIONAL PRACTICE PROBLEMS

- The surface tension of water at 20°C is $72.75 \times 10^{-3} \text{ Nm}^{-1}$. A 33.24 vol% solution of ethyl alcohol has $\gamma = 33.24 \times 10^{-3} \text{ Nm}^{-1}$ at this temperature. If $d = 0.9614 \times 10^3 \text{ kg m}^{-3}$ for the solution and $0.9982 \times 10^3 \text{ kg m}^{-3}$ for water, how much less in the same capillary tube will ethyl alcohol solution rise ?
Answer. 47.4%
- The surface tension of a liquid at 300 K is $27.1 \text{ dyne cm}^{-1}$ and its density at this temperature is 0.9880 g cm^{-3} . What is the radius of the largest capillary that will allow the liquid to rise 2.0 cm ? (Assume the angle of contact to be zero and $g = 981 \text{ cm sec}^{-2}$)
Answer. 0.028 cm
- The surface tension of water at 293 K is $72.73 \times 10^{-3} \text{ Nm}^{-2}$. How high will water rise in a capillary of diameter 0.01 cm?
Answer. 29.7 cm
- Compare the time of flow of the same volume of 20% wt. sucrose solution (density = $1.0794 \times 10^3 \text{ kg m}^{-3}$ and $\eta = 1.695$ centipoise) and 30% wt. sucrose solution (density $1.1252 \times 10^3 \text{ kg m}^{-3}$ and $\eta = 2.735$ centipoise)
Answer. time 20% wt = time 30% wt $\times 0.65$
- If light machinery oil has $\eta = 50$ centipoise and density = $0.97 \times 10^3 \text{ kg m}^{-3}$ at 298 K, how long will it take for a sample to pass through a viscometer if water under the same conditions takes 1 minute (density of water = $1.00 \times 10^3 \text{ kg m}^{-3}$ and viscosity = 0.89 centipoise).
Answer. 57.9 minutes

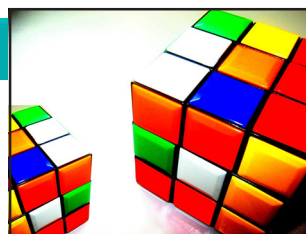
6. The refractive index of a liquid at 25 °C is 1.6 and its density is 0.87 g cm^{-3} . Find the molar refraction. (Molar mass of the liquid is 78)
Answer. $26.36 \text{ cm}^3 \text{ mol}^{-1}$
7. The molar refraction of a liquid is $12.95 \text{ cm}^3 \text{ mol}^{-1}$ and its density is 1.046 g cm^{-3} . Calculate the refractive index (molar mass of liquid is 60 g mol^{-1})
Answer. 1.369
8. Calculate the optical rotation when sodium D light passes through a solution of a compound in chloroform, containing 25 g per 100 ml, placed in a cell of 20 cm. $[\alpha]$ for the compound in chloroform is 37.5° .
Answer. 18.75°
9. The refractive index of a liquid of molar mass 72 is 1.34 and its density is 0.98 g cm^{-3} . Find its molar refraction.
Answer. $15.40 \text{ cm}^3 \text{ mol}^{-1}$
10. A glass capillary of diameter 0.1 cm is dipped into water. Calculate the level of the water that rises in the capillary if surface tension of water = $72.75 \text{ dyne cm}^{-1}$ density = 0.9984 g cm^{-3} and contact angle for water = 10° .
Answer. 2.93 cm

12

The Solid State

CHAPTER

KEY CONCEPTS AND EQUATIONS



TYPE OF SOLIDS

In the solid state the matter is incompressible. That is why it has well defined shape. The units atom or molecules or ions in solid state are in close contact and have fixed position or sites. We can classify the solids into four types on the basis of Intermolecular forces holding the structural units together.

A MOLECULAR SOLID

It consists of atoms or molecules held together by intermolecular forces. Examples are solid neon, Ice, dry ice (solid carbon dioxide), etc.

AN IONIC SOLID

It consists of cations and anions held together by the electrical attraction of oppositely charged ions (Ionic bond). Examples are CsCl, NaCl, etc.

A COVALENT NETWORK SOLID

It consists of atoms held together in large network or chains of covalent bonds. Examples are diamond, graphite, etc.

A METALLIC SOLID

It consists of positive cores of atoms held together in a "sea" of electrons (metallic bonding). Examples are – copper, iron, silver, etc.

CRYSTALLINE AND AMORPHOUS SOLIDS

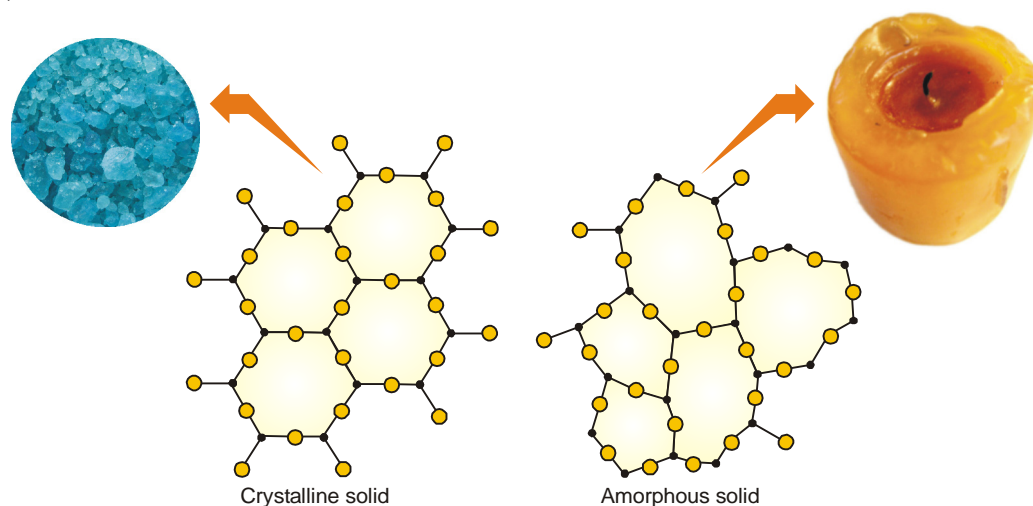
Solids may be crystalline or amorphous depending upon the arrangement of constituent units – atoms or molecules or ions.

A CRYSTALLINE SOLID

It is made up of one or more crystals and each crystal has a well-defined ordered three dimensional structure. Examples are NaCl, Sugar, etc.

AN AMORPHOUS SOLID

It has a disordered structure *i.e.* the constituent atoms, molecules or ions are arranged at random. Examples are rubber, plastic, glass, etc.



■ **Figure 12.1**

Two-dimensional representation of crystalline solid and an amorphous solid.
Each substance has the formula A_2O_3 . A is shown by • and O is shown by ○.

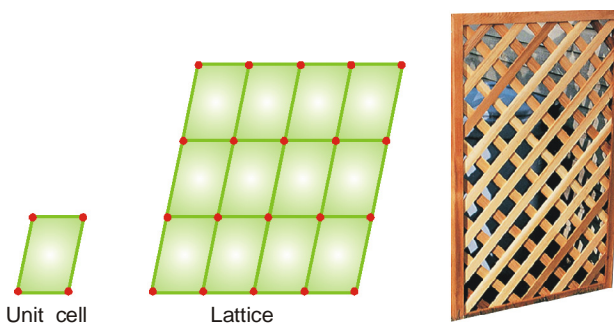
ISOTROPY AND ANISOTROPY

Amorphous substances are said to be isotropic because they exhibit the same value of any property in all directions. The refractive index, thermal and electrical conductivities, etc. are independent of the direction along which they are measured.

Crystalline substances are said to be anisotropic because the magnitude of a physical property varies with direction. For example, in a crystal of Ag I the coefficient of thermal expansion is positive in one direction and negative in the other.

CRYSTAL LATTICE

A crystal is a three dimensional ordered repeating arrangement of constituent unit atoms, molecules or ions. **A crystal lattice may be defined as the geometric arrangement of atoms or ions in space.** The position occupied by atoms or ions in the crystal lattice are called lattice sites.

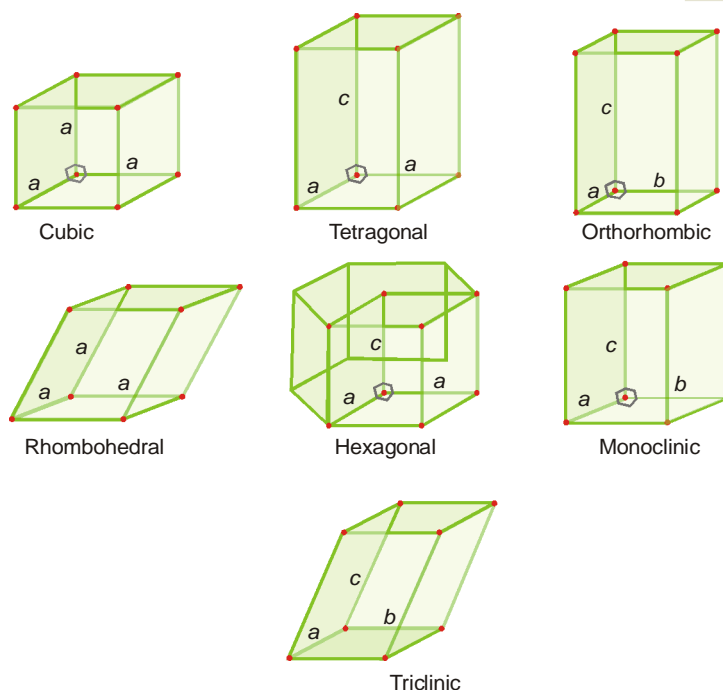


■ **Figure 12.2**

Two-dimensional illustration of unit cell and crystal lattice.

UNIT CELL

It is smallest repeating box-like unit in space lattice which when repeated over and over results in the crystal of the substance in three dimensions. It is characterised by three axes a, b and c and three angles between axes α, β and γ . Depending upon the relationship between edge lengths and angles we have seven basic shapes possible for unit cells. These are given in Table 12.1 and shown in Fig.12.3.



■ **Figure 12.3**

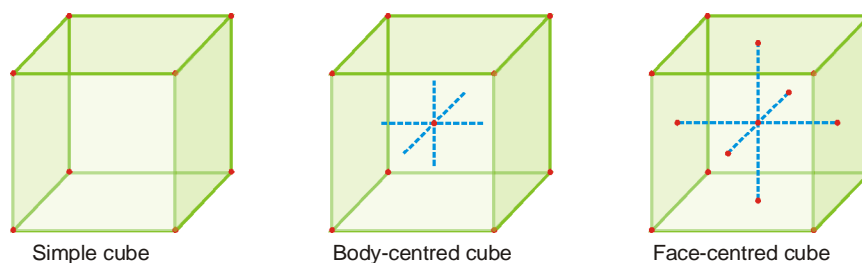
The primitive unit cells for the seven crystal systems. Where two or more of the axes are equal, the same letter is shown in each. Right angles (90°) are shown as γ . The heavy line indicates the hexagonal unit cell.

TABLE 12.1. THE SEVEN CRYSTAL SYSTEMS

Crystal	Relative Edge Length	Angles	Examples
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	Cu, NaCl, etc.
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Sn, TiO_2 , etc.
Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^\circ; \gamma \neq 90^\circ$	Borax, PbCrO_4 , etc.
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	BaSO_4 , CaCO_3 , etc.
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ; \gamma = 120^\circ$	Zinc Oxide, Graphite, etc.
Rhombohedral	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$	Calcite, HgS, etc.
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$\text{K}_2\text{Cr}_2\text{O}_7$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, etc.

CUBIC UNIT CELLS

There are three types of cubic unit cells. These are (i) Simple cubic unit cell (ii) A body centred cubic unit cell and (iii) A face centred cubic unit cell. These are shown in Fig.12.4.



■ **Figure 12.4**

Three cubic unit cells.

SIMPLE CUBIC UNIT CELL

It is the one in which the constituent units occupy only corners of a cube.

BODY CENTRED CUBIC UNIT CELL

It is the one in which there is one constituent unit at the centre of the cube in addition to the particles at the corners.

FACE CENTRED CUBIC UNIT CELL

It is the one in which there are constituent units, one each, at the six faces of the cube apart from the particles at the corners.

HOW TO DETERMINE THE NUMBER OF ATOMS IN A UNIT CELL

(i) Simple cube : Eight unit cells share each corner atom

$$\begin{aligned}\therefore \text{At each corner we have} &= 1/8 \text{ atom} \\ \text{and at 8 corners we have} &= 1/8 \text{ atom} \times 8 \\ &= 1 \text{ atom}\end{aligned}$$

(ii) Face centred cubic unit cell : Each face centred atom is shared by two units cells

$$\begin{aligned}\therefore \text{At each face we have} &= 1/2 \text{ atom} \\ \text{and at six faces we have} &= 1/2 \text{ atom} \times 6 = 3 \text{ atoms} \\ \text{at 8 corners we have} &= 1/8 \text{ atom} \times 8 = 1 \text{ atom}\end{aligned}$$

Thus the total number of atoms in face centred unit cell = 4 atoms

(iii) Body centred cubic unit cell : Each unit cell has one atom in the body

$$\begin{aligned}\therefore \text{No. of central atom} &= 1 \text{ atom} \\ \text{and at each corner we have} &= 1/8 \text{ atom} \\ \text{at 8 corners we have} &= 1/8 \text{ atom} \times 8 = 1 \text{ atom}\end{aligned}$$

Thus the total number of atom in body centred unit cell = 2 atoms

HOW TO DETERMINE MASS OF THE UNIT CELL

$$\begin{aligned}\text{Mass of the unit cell} &= \text{No. of atoms in unit cell} \times \text{Mass of one atom} \\ &= \text{No. of atoms in unit cell} \times \frac{\text{Molar mass of substance}}{\text{Avogadro's number}}\end{aligned}$$

CO-ORDINATION NUMBER OF A CRYSTAL LATTICE

The co-ordination number of a crystal lattice is the number of particles (ions, atoms or molecules) immediately adjacent to each particle in the lattice. It is the characteristic of a given space lattice. The co-ordination numbers in different types of crystal lattice are as follows :

Type of crystal lattice	Co-ordination number
Simple cube	6
Body centred cube	8
Face centred cube	12

RADIUS RATIO AND ITS RELATION WITH CO-ORDINATION NUMBER

It is defined as the ratio of cation radius to that of the anion radius. It is denoted by r_+ / r_- . It is related to the co-ordination number in the following manner

Radius ratio	Co-ordination Number
between 0.225 – 0.414	4
between 0.414 – 0.732	6
between 0.732 – 1	8

BRAGG'S EQUATION

When X-rays of wavelength λ strike the first plane at an angle θ , following equation is applicable

$$n \lambda = 2 d \sin \theta$$

where d is the distance between two successive planes, n is the order of reflection.

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. Aluminium forms face-centred cubic crystals. The density of Al is 2.70 g cm^{-3} . Calculate the length of the side of the unit cell of Al (Atomic mass of Al = 27).

SOLUTION :

Number of Al atoms in unit cell	= 4	[\therefore f c c structure]
Avogadro's number	= $6.02 \times 10^{23} \text{ mol}^{-1}$	
\therefore Mass of one Al atom	= $\frac{\text{Atomic mass}}{\text{Avogadro's number}}$	
	= $\frac{27 \text{ g mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1}}$	
	= 4.485×10^{-23}	
and Mass of one unit cell	= $4 \times 4.485 \times 10^{-23} \text{ g}$	
	= $17.940 \times 10^{-23} \text{ g}$	
Let the length of side of unit cell be	= a	
\therefore volume of the unit cell	= a^3	
and density of unit cell	= $\frac{\text{Mass}}{\text{Volume}} = 2.70 \text{ g cm}^{-3}$ (given)	
Substitution of values		
	$2.70 \text{ g cm}^{-3} = \frac{17.940 \times 10^{-23} \text{ g}}{a^3}$	
or	$a^3 = \frac{17.940 \times 10^{-23} \text{ g}}{2.70 \text{ g cm}^{-3}}$	
	$a^3 = 66.444 \times 10^{-24} \text{ cm}^3$	
or	$a = \sqrt[3]{66.444 \times 10^{-24} \text{ cm}^3}$	
	= $4.0503 \times 10^{-8} \text{ cm}$	

SOLVED PROBLEM 2. Gold has face-centred cubic structure with a unit length 4.07 \AA , a density of 19.3 g cm^{-3} . Calculate the Avogadro's number from the data (Atomic mass of Au = 197)

SOLUTION :

Number of atoms in Gold unit cell	= 4	[\therefore f c c structure]
Let Avogadro's number be	= $N_o \text{ mol}^{-1}$	
Mass of gold atom	= $\frac{\text{Atomic mass}}{\text{Avogadro's number}}$	
	= $\frac{197 \text{ g mol}^{-1}}{N_o}$	
and Mass of one gold unit cell	= $\frac{4 \times 197 \text{ g mol}^{-1}}{N_o \text{ mol}^{-1}} = \frac{788}{N_o} \text{ g}$	
Edge length of gold unit cell, a	= 4.07 \AA (given)	
	= $4.07 \times 10^{-8} \text{ cm}$	

Volume of one gold unit cell, $a^3 = (4.07 \times 10^{-8} \text{ cm})^3$

$$\therefore \text{Density} = \frac{\text{Mass}}{\text{Volume}} = \frac{\frac{788}{N_o}}{(4.07 \times 10^{-8} \text{ cm})^3} = 19.3 \text{ g cm}^{-3} \quad (\text{given})$$

Substitution of values

$$\frac{788 \text{ g}}{N_o \times (4.07 \times 10^{-8})^3 \text{ cm}^3} = 19.3 \text{ g cm}^{-3}$$

$$\begin{aligned} \text{or} \quad N_o &= \frac{788 \text{ g}}{(4.07 \times 10^{-8})^3 \times 19.3} \\ &= 0.6056 \times 10^{24} \\ &= \mathbf{6.056 \times 10^{23}} \end{aligned}$$

SOLVED PROBLEM 3. Polonium crystallises in a simple cubic unit cell. It has an atomic mass = 209 and density = 91.5 kg m^{-3} . What is the edge length of its unit cell ?

SOLUTION :

$$\text{Number of atoms of Po in unit cell} = 1 \quad [\because \text{Simple cube}]$$

$$\begin{aligned} \text{Mass of one Po atom} &= \frac{\text{Atomic mass}}{\text{Avogadro's number}} \\ &= \frac{209 \text{ g mol}^{-1}}{6.02 \times 10^{23} \text{ mol}^{-1}} \end{aligned}$$

$$= 34.7176 \times 10^{-23} \text{ g}$$

$$\text{Mass of one Po unit cell} = 1 \times 34.7176 \times 10^{-23} \text{ g} \quad [\because \text{Simple Cube} = 1 \text{ atom}]$$

$$\text{Let the length of the unit cell be} = a$$

$$\text{Volume of the unit cell} = a^3$$

$$\begin{aligned} \text{And} \quad \text{Density} &= \frac{\text{Mass}}{\text{Volume}} = 91.5 \text{ kg m}^{-3} \quad (\text{given}) \\ &= 0.0915 \text{ g m}^{-3} \end{aligned}$$

Substitution of values

$$0.0915 \text{ g cm}^{-3} = \frac{34.7176 \times 10^{-23} \text{ g}}{a^3}$$

$$\text{or} \quad a^3 = \frac{34.7176 \times 10^{-23} \text{ g}}{0.0915 \text{ g cm}^{-3}}$$

$$= 379.427 \times 10^{-23} \text{ cm}^3$$

$$= 3794.27 \times 10^{-24} \text{ cm}^3$$

$$\begin{aligned} \text{or} \quad a^3 &= \sqrt[3]{3794.27 \times 10^{-24} \text{ cm}^3} \\ &= \mathbf{15.597 \times 10^{-8} \text{ cm}} \end{aligned}$$

SOLVED PROBLEM 4. Calculate the angle at which first order diffraction will occur in an X-ray diffractometer when X-rays of wavelength 1.54 \AA are diffracted by the atoms of a crystal, given that the interplanar distance is 4.04 \AA .

SOLUTION :

Formula used

$$n \lambda = 2 d \sin \theta$$

Quantities given

$$n = 1$$

$$\lambda = 1.54 \text{ \AA}$$

$$d = 4.04 \text{ \AA}$$

Substitution of values

$$1 \times 1.54 \text{ \AA} = 2 \times 4.04 \text{ \AA} \times \sin \theta$$

$$\text{or} \quad \sin \theta = \frac{1.54 \text{ \AA}}{2 \times 4.04 \text{ \AA}}$$

$$= 0.19059$$

$$\text{or} \quad \theta = \sin^{-1} 0.19059$$

$$= 10.987^\circ$$

SOLVED PROBLEM 5. The ionic radii of Cs is 169 pm and Br is 195 pm. What kind of unit cell would be expected for CsBr crystal? Calculate the unit cell dimensions and density of CsBr crystal (atomic mass of Cs = 133; Br = 80)

SOLUTION :**(i) To find out the type of unit cell for CsBr**

$$\begin{aligned} \text{Radius ratio of CsBr Crystal, } \frac{r_+}{r_-} &= \frac{169 \text{ pm}}{195 \text{ pm}} \\ &= 0.866 \end{aligned}$$

Since the ratio lies in the range 0.732 – 1 the co-ordination number will be 8 and the crystal would exist in **simple cubic unit cell**.

(ii) To calculate the unit cell dimensions and density of CsBr

$$\begin{aligned} \text{Length of the edge of simple cube} &= 2 \times \text{radius of Br}^- \text{ ion} \\ &= 2 \times 195 \text{ pm} \\ &= 390 \text{ pm} \end{aligned}$$

$$= 390 \times 10^{-10} \text{ cm}$$

$$\text{Volume of cubic unit cell, } a^3 = (390 \times 10^{-10} \text{ cm})^3$$

$$\text{Molecular mass of CsBr} = 133 + 80 = 213 \text{ g mol}^{-1}$$

$$\begin{aligned} \text{Mass of the unit cell} &= \frac{213 \text{ g mol}^{-1}}{\text{Avogadro's Number}} \end{aligned}$$

$$= \frac{213 \text{ g mol}^{-1}}{6.023 \times 10^{23} \text{ mol}^{-1}}$$

$$= 35.3644 \times 10^{-23} \text{ g}$$

$$\begin{aligned} \text{Density of CsBr unit cell} &= \frac{\text{Mass of CsBr unit cell}}{\text{Volume of CsBr unit cell}} \end{aligned}$$

$$= \frac{35.3644 \times 10^{-23} \text{ g}}{(390 \times 10^{-10} \text{ cm})^3}$$

$$= \frac{35.3644 \times 10^7}{(390)^3} \text{ g cm}^{-3}$$

$$= 5.96 \text{ g cm}^{-3}$$

SOLVED PROBLEM 6. Platinum crystallises in a face-centred cubic lattice with all atoms at the lattice points. It has a density of 21.45 g cm^{-3} and an atomic mass of 195.08 amu. From these data, Calculate the length of a unit-cell edge.

SOLUTION :

$$\text{Molecular mass of Pt} = 195.08 \text{ amu} \quad (\text{Given})$$

$$\begin{aligned} \therefore \text{Mass of one atom of Pt} &= \frac{\text{Molecular mass}}{\text{Avogadro number}} \\ &= \frac{195.08}{6.02 \times 10^{23}} \text{ g} \\ &= 3.240 \times 10^{-22} \text{ g} \end{aligned}$$

$$\text{Number of Pt atom in unit cell} = 4 \quad [\because \text{fcc structure}]$$

$$\begin{aligned} \therefore \text{Mass of unit cell of Pt} &= 4 \times 3.240 \times 10^{-22} \text{ g} \\ &= 1.296 \times 10^{-21} \text{ g} \end{aligned}$$

$$\begin{aligned} \text{and volume of the unit cell, } V &= \frac{M}{D} = \frac{1.296 \times 10^{-21} \text{ g}}{21.45 \text{ g cm}^{-3}} \\ &= 6.042 \times 10^{-23} \text{ cm}^3 \end{aligned}$$

$$\begin{aligned} \text{Edge of the unit cell, } a &= \sqrt[3]{6.042 \times 10^{-23} \text{ cm}^3} \\ &= 3.924 \times 10^{-8} \text{ cm} \end{aligned}$$

SOLVED PROBLEM 7. A body centred cubic element of density 10.3 g cm^{-3} has a cell edge of 314 pm. Calculate the atomic mass of the element. (Avogadro's number = 6.023×10^{23})

SOLUTION :

$$\begin{aligned} \text{Number of atoms in bcc structure} &= 8 \times \frac{1}{8} + 1 \text{ atoms} \\ &= 2 \text{ atoms} \end{aligned}$$

$$\text{Density of element} = 10.3 \text{ g cm}^{-3}$$

$$\text{Edge of the unit cell, } l = 314 \text{ pm} = 314 \times 10^{-10} \text{ cm}$$

$$\therefore \text{Volume of the unit cell, } V = l^3 = (314 \times 10^{-10})^3 \text{ cm}^3$$

$$\begin{aligned} \text{Mass of the unit cell} &= \text{Density} \times \text{Volume} \\ &= 10.3 \text{ g cm}^{-3} \times (314 \times 10^{-10})^3 \text{ cm}^3 \\ &= 3.1188 \times 10^{-22} \text{ g} \end{aligned}$$

$$\begin{aligned} \text{Mass of one atom} &= \frac{3.1188 \times 10^{-22}}{2} \text{ g} \quad [\because \text{unit cell} = 2 \text{ atoms}] \\ &= 1.5594 \times 10^{-22} \text{ g} \end{aligned}$$

$$\begin{aligned} \text{Atomic mass} &= \text{Avogadro's number} \times \text{mass of 1 atom} \\ &= 6.023 \times 10^{23} \times 1.5594 \times 10^{-22} \text{ g} \\ &= 94 \text{ g mol}^{-1} \end{aligned}$$

SOLVED PROBLEM 8. A crystal of lead (II) sulphide has an NaCl structure. In this crystal the shortest distance between a Pb^{2+} ion and S^{2-} ion is 297 pm. What is the length of the edge of the unit cell in lead sulphide? Also calculate the unit cell volume ($N = 6.023 \times 10^{23} \text{ mol}^{-1}$; At. masses Pb = 207.2; S = 32)

SOLUTION :

$$\begin{aligned}
 \text{Length of the cell edge, } a &= 2(r_+ + r_-) \\
 &= 2 \times 297 \text{ pm} \\
 &= 594 \text{ pm} \\
 &= 594 \times 10^{-10} \text{ cm} \\
 \text{and volume of the unit cell, } a^3 &= (594 \times 10^{-10} \text{ cm})^3 \\
 &= 2.0958 \times 10^{-22} \text{ cm}^3
 \end{aligned}$$

SOLVED PROBLEM 9. Sodium metal crystallises in bcc lattice with cell edge $a = 4.29 \text{ \AA}$. What is the radius of sodium atom ?

SOLUTION :

We know

For a body centred cube

$$4r = \sqrt{3} a$$

or

$$\begin{aligned}
 r &= \frac{\sqrt{3}}{4} \times a \\
 &= \frac{1.73}{4} \times 4.29 \text{ \AA} \\
 &= 1.855 \text{ \AA}
 \end{aligned}$$

ADDITIONAL PRACTICE PROBLEMS

- The cell edge of a face-centred cubic element of atomic mass 108 is 409 pm. Calculate its density. (Avogadro's constant = 6.023×10^{23})
Answer: 10.48 g cm^{-3}
- A body centred cubic element of density 10.3 g cm^{-3} has a cell edge of 314 pm. Calculate the atomic mass of element. (Avogadro's constant = 6.023×10^{23})
Answer: 94 amu
- An element (atomic mass = 60) having face centred cubic structure has a density of 6.23 g cm^{-3} . What is the edge length of the unit cell. (Avogadro's constant = $6.023 \times 10^{23} \text{ mol}^{-1}$)
Answer: $4 \times 10^{-8} \text{ cm}$
- Sodium chloride crystallises in face-centred cubic (fcc) structure. Its density is 2.165 g cm^{-3} . If the distance between Na^+ and its nearest Cl^- is 281 pm, find out the Avogadro's number ($\text{Na} = 23 \text{ g mol}^{-1}$; $\text{Cl} = 35.44 \text{ g mol}^{-1}$)
Answer: $6.08 \times 10^{23} \text{ mol}^{-1}$
- Crystalline CsBr has a bcc Structure. Calculate the unit cell length if the density of CsBr crystal is 4.29 g cm^{-3} ($N_o = 6.023 \times 10^{23} \text{ mol}^{-1}$; Atomic masses, Cs = 133; Br = 80)
Answer: $4.369 \times 10^{-8} \text{ cm}$
- Lead (II) Sulphide crystal has a NaCl structure. What is its density? The edge length of the unit cell of PbS crystal is 500 pm. ($N_o = 6.023 \times 10^{23} \text{ mol}^{-1}$; Atomic masses, Pb = 207.2; S = 32)
Answer: 12.7 g cm^{-3}

7. KF has NaCl structure. What is the distance between K^+ and F^- in KF if its density is 2.48 g cm^{-3} ?
(Atomic mass of K = 39.1, F = 19)
Answer. $2.689 \times 10^{-8} \text{ cm}$
8. Sodium chloride crystal has fcc structure. Its density is $2.163 \times 10^2 \text{ kg m}^{-2}$. Calculate the edge of the unit cell cube. ($M_{NaCl} = 58.45 \times 10^{-3} \text{ kg mol}^{-1}$; $N_o = 6.023 \times 10^{23} \text{ mol}^{-1}$)
Answer. $5.640 \times 10^{-8} \text{ cm}$
9. Given for Fe $a/\text{pm} = 286$; $\rho \text{ g cm}^{-3} = 7.86$. Find the type of cubic lattice to which the crystal belongs. Also calculate the radius of Fe. (At. mass of Fe = 55.85 amu)
Answer. bcc ; 123.84 pm
10. Copper crystal has fcc cubic lattice structure. Its density is 8.93 g cm^{-3} . What is the length of the unit cell?
($N_o = 6.023 \times 10^{23}$; Atomic mass of Cu = 63.5)
Answer. $3.614 \times 10^{-8} \text{ cm}$
11. A face centred cubic element (at. mass = 60) has a unit cell edge of 400 pm. What is its density ?
($N_o = 6.023 \times 10^{23} \text{ atoms mol}^{-1}$)
Answer. 6.226 g cm^{-3}
12. Calculate the value of Avogadro's number from the data : Density of NaCl = 2.165 g cm^{-3} ; Distance between Na^+ and Cl^- in NaCl structure = 281 pm.
Answer. 6.089×10^{23}
13. The nearest neighbour distance in silver atoms in the silver crystal is $2.87 \times 10^{-10} \text{ m}$ apart. What is the density of silver ? Silver crystallizes in fcc form (Atomic mass of Ag = 108)
Answer. 10.73 g cm^{-3}
14. KF has NaCl type structure. What is the distance between K^+ and F^- in KF, if the density of KF is 2.48 g cm^{-3} ? (Atomic mass of K = 39.1 ; F = 19 ; Avogadro's Number = $6.023 \times 10^{23} \text{ mol}^{-1}$)
Answer. 268.9 pm
15. A unit cell of sodium chloride has four formula unit. The edge length of the unit cell is 0.564 nm. What is the density of sodium chloride ?
Answer. 2.1656 g cm^{-3}

13

Physical Properties and Chemical Constitution

CHAPTER

KEY CONCEPTS AND EQUATIONS



SURFACE TENSION AND CHEMICAL CONSTITUTION

The surface tension of a liquid is related to its density and density of vapour pressure at the same temperature by the relation.

$$\frac{\gamma^{1/4}}{D - d} = C$$

where γ is the surface tension, D its density and d the density of vapours at the same temperature and C is a constant. Multiplying both sides by M , the molecular mass of the liquid, we get

$$\frac{M\gamma^{1/4}}{D - d} = MC = [P]$$

The quantity $[P]$ is called parachor. As d is negligible as compared to D , the equation reduces to

$$\frac{M}{D} \gamma^{1/4} = [P]$$

or

$$V_m \gamma^{1/4} = [P]$$

or $\gamma = 1$ then

$$V_m = [P]$$

Thus **Parachor** $[P]$ may be defined as the molar volume of a liquid at a temperature that its surface tension is unity. The Parachor is very helpful in elucidating structure of molecules as it is both an additive and constitutive property.

VISCOCITY AND CHEMICAL CONSTITUTION

Viscosity is due to intermolecular attractions which resist the flow of a liquid.

If molecular volume $[M/d]$ be multiplied by the eighth root of the coefficient of viscosity, it gives a constant value $[R]$ termed as Rheochor.

$$\frac{M}{d} \times \eta^{1/8} = [R]$$

DIPOLE MOMENT

The dipole moment of a polar molecule is given by the product of the charge at one end and the distance between the opposite charges. Thus

$$\mu = q \times r$$

where q is charge in esu and r the distance is Å units (10^{-8} cm) The CGS unit for dipole moment is debye

$$\begin{aligned} 1 \text{ Debye} &= 10^{-10} \text{ esu} \times 10^{-8} \text{ cm} \\ &= 1 \times 10^{-18} \text{ esu cm} \end{aligned}$$

The dipole moment is a vector quantity. The net dipole moment of the molecule is the vector resultant of all the individual bonds.

DIPOLE MOMENT AND IONIC CHARACTER

The magnitude of the dipole moment of a diatomic molecule determines its ionic character. The % ionic character of a bond is calculated by using the formula

$$\% \text{ Ionic character} = \frac{\mu_{\text{experimental}}}{\mu_{\text{ionic}}} \times 100$$

MOLAR REFRACTION AND CONSTITUTION

The molar refraction of a molecule is a sum of contributions of the atomic refractions and bond refractions. It is helpful in elucidating the structure of molecules.

OPTICAL ACTIVITY AND CONSTITUTION

The optical activity is due to the pressure dissymmetry in the molecule. An optically active molecule exists in two or more forms which are non-superimposable mirror images of each other. These are called enantiomers. One of these enantiomers rotates the plane of polarised light towards right and is called dextro-rotatory and the other which rotates the plane of polarised light towards left is called leavorotatory.

MAGNETIC PROPERTIES

Substances can be classified as Diamagnetic or Paramagnetic depending upon their behaviour in a magnetic field.

Diamagnetic substances are slightly repelled or pushed out of magnetic field, and

Paramagnetic substances are slightly attracted or pulled into the magnetic field.

Paramagnetism is due to the presence of unpaired electrons in the ion or molecule whereas all electrons are paired in Diamagnetic substances.

The magnetic moment of a molecule is given by the formula

$$\mu = \sqrt{n(n+2)}$$

where μ is magnetic moment in magnetons and n is the number of unpaired electrons.

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. Parachor of decane is found to be 424.2. Each $-\text{CH}_2-$ group has a parachor value of 39. Find out the parachor of hydrogen and carbon.

SOLUTION :

Formula used

$$\text{Parachor of decane} = 2 \times \text{Parachor of } \text{CH}_3- + 8 \times \text{Parachor of } \text{CH}_2-$$

Quantities given

$$\text{Parachor of decane} = 424.2$$

$$\text{Parachor of } -\text{CH}_2- = 39$$

Substitution of values

$$424.2 = 2 \times \text{Parachor of } \text{CH}_3- + 8 \times 39$$

or

$$2 \times \text{Parachor of } \text{CH}_3- = 424.2 - 8 \times 39$$

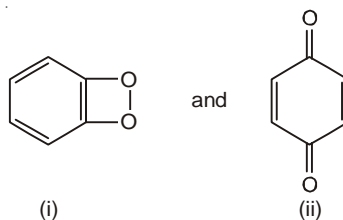
or

$$\text{Parachor of } \text{CH}_3- = \frac{112.2}{2} = 56.1$$

$$\begin{aligned} \text{Parachor of } \text{H} &= \text{Parachor of } \text{CH}_3- - \text{Parachor of } -\text{CH}_2- \\ &= 56.1 - 39 = 17.1 \end{aligned}$$

$$\begin{aligned} \text{Parachor of } \text{C} &= \text{Parachor of } \text{CH}_3- - 3 \times \text{Parachor of } \text{H} \\ &= 56.1 - 3 \times 17.1 \\ &= 4.8 \end{aligned}$$

SOLVED PROBLEM 2. For quinone, the following two structures are proposed :



The experimental value of parachor of quinone is 237.0. Parachor values for $H = 17.1$, $C = 4.8$, $O = 20.0$, double bond = 23.2, 6-carbon ring = 6.1. Which constitution will you accept ?

SOLUTION :

$$\begin{aligned} \text{Parachor of Structure (i)} &= 6 \times P_C + 4 \times P_H + 2 \times P_O + P_{\text{carbon ring}} + 3 \times P_{\text{double bond}} \\ &= 6 \times 4.8 + 4 \times 17.1 + 2 \times 20.0 + 6.1 + 3 \times 23.2 \\ &= 212.9 \end{aligned}$$

$$\begin{aligned} \text{Parachor of structure (ii)} &= 6 \times P_C + 4 \times P_H + 2 \times P_O + P_{\text{carbon ring}} + 4 \times P_{\text{double bond}} \\ &= 6 \times 4.8 + 4 \times 17.1 + 2 \times 20 + 6.1 + 4 \times 23.2 \\ &= 28.8 + 68.4 + 40 + 6.1 + 92.8 \\ &= 236.1 \end{aligned}$$

The value of Parachor structure (ii) is close to the experimental value. Thus the structure (ii) is accepted.

SOLVED PROBLEM 3. Predict the parachor for $\text{CH}_3-\text{C}_6\text{H}_4-\text{CN}$ if the parachor equivalent for C is 4.8 ; H , 17.1 ; N , 12.5 ; double bond, 23.2 ; triple Bond, 46.6 ; and six-membered ring, 6.1.

SOLUTION :

The predicted parachor is the sum of the equivalents *i.e.*

$$\begin{aligned} 8 \text{ C} &= 8 \times 4.8 = 38.4 \\ 7 \text{ H} &= 7 \times 17.1 = 119.7 \\ 1 \text{ N} &= 1 \times 12.5 = 12.5 \\ \text{One six membered ring} &= 1 \times 6.1 = 6.1 \\ \text{Triple bond (one)} &= 1 \times 46.6 = 46.6 \\ \text{Three double bonds} &= 3 \times 23.2 = 69.6 \\ \text{Total} &= \underline{\underline{292.9}} \end{aligned}$$

SOLVED PROBLEM 4. The density of hexane at 25 °C is 0.6874 g cm⁻³. Calculate the surface tension of hexane if the parachors of ethane and propane are 110.5 and 150.8 respectively.

SOLUTION :

(i) To calculate the parachor of C₆H₁₄

$$\begin{aligned} [P]_{C_2H_6} &= 2 \times [P]_{CH_3} = 110.5 \\ [P]_{C_3H_8} &= 2 \times [P]_{CH_3} + [P]_{CH_2} = 150.8 \\ \therefore [P]_{CH_2} &= [P]_{C_3H_8} - [P]_{C_2H_6} \\ &= 150.8 - 110.5 = 40.3 \\ [P]_{C_6H_{14}} &= [P]_{C_3H_8} + 3 \times [P]_{CH_2} \\ &= 150.8 + 3 \times 40.3 \\ &= 271.7 \end{aligned}$$

$$\text{Molar mass of Hexane} = 86$$

(ii) To calculate the surface tension of C₆H₁₄

Formula used

$$\frac{M}{D} \gamma^{1/4} = [P]$$

Quantities given

$$[P] = 271.7$$

$$M = 86$$

$$D = 0.6874 \text{ g cm}^{-3}$$

Substitution of values

$$\frac{86}{0.6874} \times \gamma^{1/4} = 271.7$$

$$\text{or } \gamma^{1/4} = \frac{271.7 \times 0.6874}{86} \text{ dyne cm}^{-1}$$

$$\gamma^{1/4} = 2.172 \text{ dynes cm}^{-1}$$

$$\begin{aligned} \text{and } \gamma &= (2.172)^4 \text{ dynes cm}^{-1} \\ &= \mathbf{22.25 \text{ dyne cm}^{-1}} \end{aligned}$$

SOLVED PROBLEM 4. The density of paraldehyde is 0.9943 g cm⁻³. Calculate the parachor if the surface tension is 25.9 dyne cm⁻¹. The molar mass of paraldehyde is 132.16 g mol⁻¹.

SOLUTION :

Formula used

$$\frac{M}{D} \gamma^{1/4} = [P]$$

Quantities given

$$M = 132.16 \text{ g mol}^{-1}$$

$$D = 0.9943 \text{ g cm}^{-3}$$

$$\gamma = 25.9 \text{ dyne cm}^{-1}$$

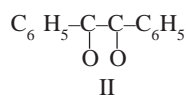
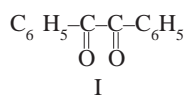
Substitution of values

$$\begin{aligned} [P] &= \frac{132.16}{0.9943} \times (25.9)^{1/4} \\ &= 132.91 \times 2.256 \\ &= \mathbf{299.84} \end{aligned}$$

ADDITIONAL PRACTICE PROBLEMS

- The parachor equivalent for C is 4.8; for H, 17.1 ; and for O, 20.0 Calculate the parachor for methanol.
Answer. 93.2
- The parachor equivalents for C is 4.8 ; for H, 17.1 ; and for O, 20.0. Calculate the parachor for ethyl alcohol.
Answer. 132.2
- Calculate the parachors of methanol and ethanol if $\gamma = 22 \times 10^{-3} \text{ Nm}^{-1}$ for each alcohol and if $d = 0.7914 \times 10^3 \text{ kg m}^{-3}$ for methanol and $0.7893 \times 10^3 \text{ kg m}^{-3}$ for ethanol.
Answer. 87.6 and 126.2

- For benzil, the following two structures have been proposed



The experimental value of parachor of quinone is 479. Parachor values for H = 17.1, C = 4.8, O = 20., double bond = 23.2, 6-carbon ring = 6.1. Which constitution will you accept ?

Answer. I

- A substance having the molecular formula $\text{C}_3\text{H}_6\text{O}$ may be allyl alcohol ($\text{CH}_2=\text{CH}-\text{CH}_2-\text{OH}$) or acetone ($\text{CH}_3-\text{CO}-\text{CH}_3$). Determine the correct formula if the observed molar refractivity of the compound is $15.998 \text{ cm}^3 \text{ mol}^{-1}$. Given that refractivities of C = 2.418, H = 1.100, O (Carbonyl) = 2.211, O (hydroxyl) = 1.525 and C = C double bond = 1.733.

Answer. 16.06 acetone

- For isocyanide, the following two structures have been suggested



The experimental value of parachor of quinone is 65. Parachor values for N = 12.5, C = 4.8, double bond 23.2. Which constitution will you accept ?

Answer. II

- The molecule AsF_3 has a dipole moment of 2.59 D. Which of following geometries are possible?
Trigonal planar, Trigonal pyramidal, T-shaped
Answer. Trigonal pyramidal
- Which of the following molecules would be expected to have zero dipole moments on the basis of their geometry ? (a) H_2S (b) PF_3 (c) TeF_6 (d) BeF_2
Answer. (c) and (d)
- Calculate the %age ionic character of H – Cl bond if the distance between the two atoms is 1.275 \AA and its dipole moment is 1.03 D.

Answer. 16.885%

- Each of the following molecules has a non zero dipole moment. Select the geometry that is consistent with this information.

(a) SO_2 ; Linear, Bent

(b) PH_3 ; Trigonal planar, Trigonal pyramidal

Answer. (a) Bent (b) Trigonal pyramidal

14

Solutions

CHAPTER

KEY CONCEPTS AND EQUATIONS



SOLUTION AND ITS CONCENTRATION

A solution is a homogeneous mixture of two or more substances. The substance which is present in smaller amount is called a **solute** and the one which is present in a large amount is called **solvent**. The concentration of a solution is the amount of solute present in a given amount of solution *i.e.*

$$\text{Concentration} = \frac{\text{Amount of solute}}{\text{Volume of solution}}$$

WAYS OF EXPRESSING CONCENTRATION

(i) Percent by weight

It is the weight of solute as a per cent of the total weight of the solution *i.e.*

$$\% \text{ by weight of solute} = \frac{\text{Weight of solute}}{\text{Weight of solution}} \times 100$$

(ii) Mole Fraction

It is the ratio of number of moles of solute and the total number of moles of solute and solvent. Thus

$$X_{\text{solute}} = \frac{\text{moles of solute}}{\text{moles of solute} + \text{moles of solvent}}$$

$$X_{\text{solute}} = \frac{n}{n + N} \quad \text{and} \quad X_{\text{solvent}} = \frac{N}{n + N}$$

Where n is the number of moles of solute and N the number of moles of solvent.

(iii) Molarity

It is the number of moles of solute per litre of solution.

$$\text{i.e.} \quad \text{Molarity, } M = \frac{\text{moles of solute}}{\text{volume of solution in litres}}$$

(iv) Molality

It is the number of solute per kilogram of solvent *i.e.*

$$\text{Molality, } m = \frac{\text{moles of solute}}{\text{mass of solvent in kg}}$$

(v) Normality

It is defined as the number of gram equivalents of solute per litre of solution. Thus

$$\text{Normality, } N = \frac{\text{no. of gram equivalents of solute}}{\text{volume of solution in litres}}$$

(vi) Formality

It is the number of formula weight in grams dissolved per litre of solution. When formula weight is equal to the molecular weight, the formality and molarity are the same.

SOLUTION OF GASES IN GASES

When two gases which do not react chemically are mixed, a homogeneous solution is obtained. Such a mixture follows Dalton's law of partial pressure.

HENRY'S LAW

The solubility of a gas in a solvent depends upon the pressure and temperature. The effect of pressure on solubility of a gas can be predicted quantitatively by Henry's law which states that the solubility of a gas is directly proportional to the partial pressure of the gas above the solution. Mathematically,

$$C \propto P \quad \text{or} \quad C = kP$$

where C is the concentration of the gas in solution, k , the proportionality constant and P , the pressure of the gas.

VAPOUR PRESSURE OF MIXTURE OF NON-MISCIBLE LIQUIDS

In a mixture of non-miscible liquids, each component exerts its own vapour pressure independent of others and the total vapour pressure is equal to the sum of individual vapour pressures of all the liquids. This generalisation is the basic principle of steam distillation. The number of molecules of each component in the vapour will be proportional to its vapour pressure i.e. to the vapour pressure of the pure liquid at that temperature. Hence

$$\frac{n_1}{n_2} = \frac{p_1}{p_2}$$

where n_1 and n_2 are the number of moles of the two components, p_1 and p_2 are their vapour pressures.

We can also write

$$\frac{w_1 / M_1}{w_2 / M_2} = \frac{p_1}{p_2}$$

where w_1 and w_2 are the masses of two liquids with their molecular masses M_1 and M_2 respectively. From this we can calculate the molecular mass of one component if that of other is given.

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. Calculate the molality of a solution of sodium hydroxide which contains 0.2 g of sodium hydroxide in 50 g of the solvent.

SOLUTION :**Formula used**

$$\text{Molality, } m = \frac{\text{No. of moles of solute}}{\text{mass of solvent in kg}}$$

Quantities given

$$\text{amount of NaOH} = 0.2 \text{ g and no. of moles of NaOH} = \frac{0.2 \text{ g}}{40 \text{ g mol}^{-1}}$$

$$\text{mass of solvent} = 50 \text{ g} = 50 \times 10^{-3} \text{ kg} = 0.005 \text{ kg}$$

Substitution of values

$$\begin{aligned}\text{Molality, } m &= \frac{0.005}{50 \times 10^{-3}} \\ &= \mathbf{0.1\ m}\end{aligned}$$

SOLVED PROBLEM 2. Calculate the normality of a solution containing 6.3 g of oxalic acid crystals (molecular mass = 126) dissolved in 500 ml of the solution.

Formula used

$$\text{Normality, } N = \frac{\text{No. of gram equivalents}}{\text{volume of solution in litres}}$$

Quantities given

$$\text{Amount of oxalic acid in 500 ml solution} = 6.3\ \text{g}$$

$$\begin{aligned}\text{No. of gram equivalents of oxalic acid} &= \frac{\text{Amt. of solute}}{\text{gram equivalent weight}} \\ &= \frac{6.3\ \text{g}}{63\ \text{g equiv}^{-1}} \\ &= 0.1\ \text{equiv}\end{aligned}$$

$$\text{volume of solution} = 500\ \text{ml} = 0.5\ \text{lit.}$$

Substitution of values

$$\begin{aligned}\text{Normality, } N &= \frac{0.1}{0.5} \\ &= \mathbf{0.2\ N}\end{aligned}$$

SOLVED PROBLEM 3. A sample of spirit contains 92% ethanol by weight, the rest being water. What is the mole fraction of its constituents ?

SOLUTION :

$$\text{Let the weight of a sample of ethanol be} = 100\ \text{g}$$

$$\text{Amount of ethanol in the sample} = 92\ \% = 92\ \text{g}$$

$$\text{and Amount of water in the sample} = 8\ \% = 8\ \text{g}$$

Formula used

$$X_A = \frac{\text{No. of moles of A}}{\text{Total no. of moles}}$$

Quantities given

$$\text{No. of moles of ethanol} = \frac{\text{Amount}}{\text{Molar mass}} = \frac{92\ \text{g}}{46\ \text{g mol}^{-1}} = 2\ \text{moles}$$

$$\text{No. of moles of water} = \frac{\text{Amount}}{\text{Molar mass}} = \frac{8\ \text{g}}{18\ \text{g mol}^{-1}} = 0.444\ \text{mole}$$

Substitution of values

$$X_{\text{ethanol}} = \frac{2\ \text{moles}}{2\ \text{moles} + 0.444\ \text{mole}} = \frac{2\ \text{mole}}{2.444\ \text{mole}} = \mathbf{0.818}$$

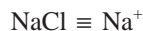
and

$$X_{\text{H}_2\text{O}} = \frac{0.444\ \text{mole}}{2\ \text{moles} + 0.444\ \text{mole}} = \frac{0.444\ \text{mole}}{2.444\ \text{mole}} = \mathbf{0.182}$$

SOLVED PROBLEM 4. Calculate the ionic strength of a solution containing 0.2 M NaCl and 0.1 M Na₂SO₄.

SOLUTION :

Since



$$\text{Amount of Na}^+ \text{ from } 0.2\ \text{M NaCl} = 0.2 \times \text{Atomic mass of Na}^+$$

$$\begin{aligned}
 &= 0.2 \times 23 \\
 &= 4.6 \text{ g lit}^{-1} \\
 \text{and} \quad \text{Na}_2\text{SO}_4 &\equiv 2 \text{ Na}^+ \\
 \text{Amount of Na}^+ \text{ from } 0.1 \text{ M Na}_2\text{SO}_4 &= 2 \times 0.1 \times \text{Atomic mass of Na}^+ \\
 &= 2 \times 0.1 \times 23 \\
 &= 4.6 \text{ g lit}^{-1} \\
 \text{Thus total strength of Na}^+ \text{ ions} &= 4.6 \text{ g lit}^{-1} + 4.6 \text{ g lit}^{-1} \\
 &= \mathbf{9.2 \text{ g lit}^{-1}} \\
 \text{Now} \quad \text{NaCl} &\equiv \text{Cl}^- \\
 \text{Amount of Cl}^- \text{ from } 0.2 \text{ M NaCl} &= 0.2 \times \text{Formula mass of Cl}^- \\
 &= 0.2 \times 35.5 \\
 &= \mathbf{7.1 \text{ g lit}^{-1}} \\
 \text{and Amount of SO}_4^{2-} \text{ from } 0.1 \text{ M Na}_2\text{SO}_4 &= 0.1 \times \text{Formula mass of SO}_4^{2-} \\
 &= 0.1 \times 96 \\
 &= \mathbf{9.6 \text{ g lit}^{-1}}
 \end{aligned}$$

SOLVED PROBLEM 5. Determine the molality of a solution containing 86.53 g of sodium carbonate (molar mass = 105.99) per litre in water at 20°C. The density of the solution at this temperature is 1.0816 g ml⁻¹.

SOLUTION :

(i) To calculate the amount of Na₂CO₃ in 1000 g of water

$$\begin{aligned}
 \text{Density of solution} &= 1.0816 \text{ g ml}^{-1} \\
 \therefore \text{Mass of 1 litre solution} &= 1.0816 \text{ g ml}^{-1} \times 1000 \text{ ml} \quad [\because M = \text{density} \times \text{vol.}] \\
 &= 1081.6 \text{ g} \\
 \text{Amt. of sodium carbonate in 1081.6 g of} &= 86.53 \text{ g (given)} \\
 \therefore \text{Amt. of Na}_2\text{CO}_3 \text{ in 1000 g of water} &= \frac{86.53 \times 1000}{1081.6} \text{ g} \\
 &= 80.0 \text{ g}
 \end{aligned}$$

(ii) To calculate the molality

Formula used

$$\text{Molality, } m = \frac{\text{Amount of Na}_2\text{CO}_3 \text{ in 1000 g of water}}{\text{molar mass}}$$

Quantities given

$$\begin{aligned}
 \text{Amount of Na}_2\text{CO}_3 \text{ in 1000 g of water} &= 80.0 \text{ g} \\
 \text{Molar mass of Na}_2\text{CO}_3 &= 105.99 \text{ g mol}^{-1}
 \end{aligned}$$

Substitution of values

$$\begin{aligned}
 \text{Molality, } m &= \frac{80 \text{ g}}{105.99 \text{ g mol}^{-1}} \\
 &= \mathbf{0.7548 \text{ m}}
 \end{aligned}$$

SOLVED PROBLEM 6. A solution contains 25% water, 25% ethanol and 50% ethanoic acid. Calculate the mole fraction of each component.

SOLUTION :

(i) To calculate the total number of moles

$$\text{Let the mass of solution be} = 100 \text{ g}$$

$$\begin{aligned}
 \text{Amount of H}_2\text{O} &= 25\% = 25 \text{ g} \\
 \text{Amount of C}_2\text{H}_5\text{OH} &= 25\% = 25 \text{ g} \\
 \text{Amount of CH}_3\text{COOH} &= 50\% = 50 \text{ g} \\
 \text{Number of moles of water} &= \frac{25 \text{ g}}{18 \text{ g mol}^{-1}} = 1.3888 \text{ moles} \\
 \text{Number of moles of C}_2\text{H}_5\text{OH} &= \frac{25 \text{ g}}{46 \text{ g mol}^{-1}} = 0.5435 \text{ mole} \\
 \text{Number of moles of CH}_3\text{COOH} &= \frac{50 \text{ g}}{60 \text{ g mol}^{-1}} = 0.8333 \text{ moles} \\
 \text{Total number of moles} &= 1.3888 + 0.5434 + 0.8333 \text{ moles} \\
 &= 2.7655 \text{ moles}
 \end{aligned}$$

(ii) To calculate the mole fraction of each component**Formula used**

$$X_{\text{Component}} = \frac{\text{No. of moles of component}}{\text{Total no. of moles}}$$

Substitution of values

$$\begin{aligned}
 \text{Mole fraction of H}_2\text{O}, X_{\text{H}_2\text{O}} &= \frac{1.3888 \text{ moles}}{2.7655 \text{ moles}} = \mathbf{0.502} \\
 \text{Mole Fraction of C}_2\text{H}_5\text{OH}, X_{\text{C}_2\text{H}_5\text{OH}} &= \frac{0.5435 \text{ mole}}{2.7655 \text{ moles}} = \mathbf{0.1965} \\
 \text{Mole Fraction of CH}_3\text{COOH}, X_{\text{CH}_3\text{COOH}} &= \frac{0.8333 \text{ mole}}{2.7655 \text{ mole}} = \mathbf{0.3013}
 \end{aligned}$$

SOLVED PROBLEM 7. What is molarity and molality of a 13% solution (by weight) of sulphuric acid? Its density is 1.09 g ml^{-1} .

SOLUTION :

$$\begin{aligned}
 \text{Let the mass of solution be} &= 100 \text{ g} \\
 \text{Amount of H}_2\text{SO}_4 \text{ in solution} &= 13 \text{ g} \\
 \text{Amount of H}_2\text{O in solution} &= 87 \text{ g} \\
 \text{Number of moles of H}_2\text{SO}_4 &= \frac{13 \text{ g}}{98 \text{ g mol}^{-1}} = 0.1326 \text{ mol}
 \end{aligned}$$

(i) To calculate the molality**Formula used**

$$\text{Molality, } m = \frac{\text{No. of moles of H}_2\text{SO}_4}{\text{Mass of solvent in kg}}$$

Quantities given

$$\begin{aligned}
 \text{No. of moles H}_2\text{SO}_4 &= 0.1326 \\
 \text{Mass of solvent} &= 87 \text{ g} = 87 \times 10^{-3} \text{ kg}
 \end{aligned}$$

Substitution of value

$$\begin{aligned}
 \text{Molality, } m &= \frac{0.1326}{87 \times 10^{-3} \text{ kg}} \\
 &= \mathbf{1.524 \text{ m}}
 \end{aligned}$$

(ii) To calculate the molarity

$$\text{Volume of 100 g of solution} = \frac{\text{Mass}}{\text{Density}} = \frac{100 \text{ g}}{1.09 \text{ g ml}^{-1}}$$

$$\begin{aligned}
 &= 91.74 \text{ ml} \\
 &= 0.09174 \text{ lit} \\
 \text{Molarity, } M &= \frac{\text{No. of moles of H}_2\text{SO}_4}{\text{Volume of solution in litre}} \\
 &= \frac{0.1326}{0.09174} \\
 &= \mathbf{1.4459 \text{ M}}
 \end{aligned}$$

SOLVED PROBLEM 8. 49 g of H_2SO_4 are dissolved in 250 ml of solution. Calculate the molarity of the solution.

Solution :

$$\begin{aligned}
 \text{Amount of H}_2\text{SO}_4 \text{ in 250 ml solution} &= 49 \text{ g} \\
 \text{Amount of H}_2\text{SO}_4 \text{ in 1 lit solution} &= \frac{49 \times 1000}{250} \text{ g} \\
 &= 196 \text{ g} \\
 \text{No. of moles of H}_2\text{SO}_4 \text{ in 1 lit solution} &= \frac{196 \text{ g}}{98 \text{ g mol}^{-1}} \\
 &= 2 \text{ moles} \\
 \text{Molarity, } M &= \frac{\text{No. of moles of H}_2\text{SO}_4}{\text{Volume of solution in litre}} \\
 &= \frac{2 \text{ moles}}{1 \text{ lit}} \\
 &= \mathbf{2 \text{ M}}
 \end{aligned}$$

SOLVED PROBLEM 9. 45 g of glucose, $\text{C}_6\text{H}_{12}\text{O}_6$, are dissolved in 500 g of water. Calculate the molality of the solution.

SOLUTION :

$$\begin{aligned}
 \text{Amount of glucose in 500 g water} &= 45 \text{ g} \\
 \text{No. of moles of glucose in 500 g water} &= \frac{45 \text{ g}}{180 \text{ g mol}^{-1}} \\
 &= 0.25 \text{ mol} \\
 \text{Mass of water} &= 500 \text{ g} \\
 &= 500 \times 10^{-3} \text{ kg} \\
 \text{Molality, } m &= \frac{\text{No. of moles of glucose}}{\text{Mass of water in kg}} \\
 &= \frac{0.25}{500 \times 10^{-3}} \\
 &= \mathbf{0.5 \text{ m}}
 \end{aligned}$$

SOLVED PROBLEM 10. Nitrobenzene is completely miscible with water. A mixture of two liquids boils at 99°C and 753 torr pressure. The vapour pressure of water is 733 torr at this temperature. Find out the weight composition of liquid mixture.

SOLUTION :

Formula used

$$\frac{w_1}{w_2} = \frac{p_1}{p_2} \times \frac{M_1}{M_2}$$

Quantities given

$$\begin{aligned}
 p_1 &= \text{Vap. pressure of mixture} - \text{vap. pressure of water} \\
 &= 753 \text{ torr} - 733 \text{ torr} \\
 &= 20 \text{ torr}
 \end{aligned}$$

$$P_2 = 733 \text{ torr}$$

$$M_1 \text{ of Nitrobenzene (C}_6\text{H}_5\text{NO}_2) = 123$$

$$M_2 \text{ of water} = 18$$

Substitution of values

$$\begin{aligned}
 \frac{w_1}{w_2} &= \frac{20 \text{ torr}}{733 \text{ torr}} \times \frac{123}{18} \\
 &= 5.36
 \end{aligned}$$

$$\frac{w_1}{w_2} = \frac{5.36}{1}$$

or

$$w_1 : w_2 = 5.36 : 1$$

SOLVED PROBLEM 11. Calculate the mole fraction of water in a mixture of 12 g of water, 108 g of acetic acid and 92 g of ethyl alcohol.

SOLUTION :**(i) To calculate the total number of moles**

$$\begin{aligned}
 \text{No. of moles of H}_2\text{O} &= \frac{12 \text{ g}}{18 \text{ g mol}^{-1}} = 0.667 \text{ mole} \\
 \text{No. of moles of CH}_3\text{COOH} &= \frac{108 \text{ g}}{60 \text{ g mol}^{-1}} = 1.80 \text{ mole} \\
 \text{No. of moles of C}_2\text{H}_5\text{OH} &= \frac{92 \text{ g}}{46 \text{ g mol}^{-1}} = 2.0 \text{ mole} \\
 \text{Total number of moles} &= 0.667 \text{ moles} + 1.80 \text{ moles} + 2.0 \text{ moles} \\
 &= 4.467 \text{ moles}
 \end{aligned}$$

(ii) To calculate the mole fraction of H₂O**Formula used**

$$\begin{aligned}
 X_{\text{H}_2\text{O}} &= \frac{\text{Number of moles of H}_2\text{O}}{\text{Total number of moles}} \\
 &= \frac{0.667 \text{ mole}}{4.467 \text{ mole}} \\
 &= \mathbf{0.1493}
 \end{aligned}$$

SOLVED PROBLEM 12. Calculate the molality of 1M solution of sodium nitrate, the density of solution is 1.25 g cm^{-3} .

SOLUTION :

$$\begin{aligned}
 \text{Mass of 1 litre solution of NaNO}_3 &= \text{Density} \times \text{volume} \\
 &= 1.25 \text{ g cm}^{-3} \times 1000 \text{ cm}^3 \\
 &= 1250 \text{ g} \\
 \text{Molar mass of NaNO}_3 &= 23 + 14 + 48 = 85 \text{ g mol}^{-1} \\
 \text{Mass of water in one litre solution} &= 1250 \text{ g} - 85 \text{ g} \\
 &= 1165 \text{ g} \\
 &= 1.165 \text{ kg} \\
 \text{Molality of NaNO}_3 &= \frac{\text{Number of moles of NaNO}_3}{\text{Mass of water in kg}}
 \end{aligned}$$

$$= \frac{1 \text{ mole}}{1.165 \text{ kg}}$$

$$= \mathbf{0.8583 \text{ m}}$$

SOLVED PROBLEM 13. 2.82 g of glucose (mol mass = 180) are dissolved in 30 g of water.

Calculate the (i) molality of the solution (ii) mole fraction of glucose and water.

SOLUTION :

(i) To calculate the molality of the solution

$$\begin{aligned} \text{Number of moles of glucose} &= \frac{\text{mass of glucose}}{\text{molar mass}} \\ &= \frac{2.82 \text{ g}}{180 \text{ g mol}^{-1}} = 0.01567 \\ \text{Amount of solvent} &= 30 \text{ g} = 30 \times 10^{-3} \text{ kg} \\ \text{Molality of glucose, } m &= \frac{\text{No. of moles of glucose}}{\text{amt. of water in kg}} \\ &= \frac{0.01567}{30 \times 10^{-3}} \\ &= \mathbf{0.5223 \text{ m}} \end{aligned}$$

(ii) To calculate the mole fraction of glucose and water

$$\begin{aligned} \text{No. of moles of H}_2\text{O} &= \frac{30 \text{ g}}{18 \text{ g mol}^{-1}} = 1.6667 \text{ mole} \\ \text{Number of moles of glucose} &= 0.01567 \text{ mole} \\ \text{Total number of glucose} &= 0.01567 + 1.6667 \text{ mole} \\ &= 1.68237 \end{aligned}$$

Formula used

$$\begin{aligned} X_{\text{component}} &= \frac{\text{No. of moles of component}}{\text{Total number of moles}} \\ X_{\text{glucose}} &= \frac{0.01567 \text{ mole}}{1.68237 \text{ mole}} = \mathbf{0.0093} \\ X_{\text{H}_2\text{O}} &= \frac{1.6667 \text{ mole}}{1.68237 \text{ mole}} = \mathbf{0.9907} \end{aligned}$$

SOLVED PROBLEM 14. Calculate the mole fraction of ethyl alcohol in a solution of total volume 86 ml prepared by adding 50 ml of ethyl alcohol ($d = 0.789 \text{ g ml}^{-1}$) to 50 ml of water (density = 1.0 g ml^{-1})

SOLUTION :

$$\begin{aligned} \text{Mass of 50 ml ethyl alcohol} &= \text{Density} \times \text{volume} = 0.789 \text{ g ml}^{-1} \times 50 \text{ ml} \\ &= 39.45 \text{ g} \\ \text{Number of moles of C}_2\text{H}_5\text{OH} &= \frac{\text{Amt of C}_2\text{H}_5\text{OH}}{\text{molar mass of C}_2\text{H}_5\text{OH}} = \frac{39.45 \text{ g}}{46 \text{ g mol}^{-1}} \\ &= 0.8576 \text{ mole} \\ \text{Mass of 50 ml of water} &= \text{Density} \times \text{volume} \\ &= 1.0 \text{ g ml}^{-1} \times 50 \text{ ml} \\ &= 50 \text{ g} \\ \text{Number of moles of H}_2\text{O} &= \frac{50 \text{ g}}{18 \text{ g mol}^{-1}} = 2.777 \text{ moles} \end{aligned}$$

$$\begin{aligned}
 \text{Mole fraction of ethyl alcohol, } X_{C_2H_5OH} &= \frac{\text{No. of moles } C_2H_5OH}{\text{Total no. of moles}} \\
 &= \frac{0.8576 \text{ mole}}{0.8576 \text{ mole} + 2.777 \text{ moles}} \\
 &= \mathbf{0.2359}
 \end{aligned}$$

SOLVED PROBLEM 15. The density of a 3 M sodium thiosulphate solution is 1.25 g ml⁻¹. Calculate (i) the % by weight of sodium thiosulphate, (ii) the mole fraction of sodium thiosulphate, and (iii) the molality of Na⁺ and S₂O₃²⁻ ions.

SOLUTION :

(i) To calculate the % by weight of sodium thiosulphate

$$\begin{aligned}
 \text{Density of the solution} &= 1.25 \text{ g ml}^{-1} \\
 \text{Mass of 1000 ml of solution} &= \text{Density} \times \text{volume} \\
 &= 1.25 \text{ g ml}^{-1} \times 1000 \text{ ml} = 1250 \text{ g} \\
 \text{Amt of Na}_2\text{S}_2\text{O}_3 \text{ in 3 M solution} &= 3 \times \text{molar mass of Na}_2\text{S}_2\text{O}_3 \\
 &= 3 \times 158 \text{ g} \\
 &= 474 \text{ g} \\
 1250 \text{ g of solution contains Na}_2\text{S}_2\text{O}_3 &= 474 \text{ g} \\
 \% \text{ by weight of Na}_2\text{S}_2\text{O}_3 &= \frac{474 \text{ g}}{1250 \text{ g}} \times 100 \\
 &= \mathbf{37.92 \%}
 \end{aligned}$$

(ii) To calculate the mole fraction of Na₂S₂O₃

$$\begin{aligned}
 \text{Amount of Na}_2\text{S}_2\text{O}_3 \text{ in 100g solution} &= 37.92 \\
 \text{Amount of H}_2\text{O in 100 g solution} &= 100 - 37.92 = 62.08 \text{ g} \\
 \text{Number of moles of Na}_2\text{S}_2\text{O}_3 &= \frac{37.92 \text{ g}}{158 \text{ g mole}} = 0.24 \text{ mole} \\
 \text{Number of moles of water} &= \frac{62.08 \text{ g}}{18 \text{ g mol}^{-1}} = 3.449 \text{ mol} \\
 \text{Total no. of moles} &= 0.24 \text{ mole} + 3.449 \text{ mole} = 3.689 \text{ moles} \\
 \text{Mole fraction of Na}_2\text{S}_2\text{O}_3, X_{Na_2S_2O_3} &= \frac{0.24 \text{ mole}}{3.689 \text{ mole}} = \mathbf{0.065}
 \end{aligned}$$

(iii) To calculate molality of Na⁺ and S₂O₃²⁻ ions

$$\begin{aligned}
 \text{No. of moles of Na}_2 \text{ in 68.02 g water} &= 0.24 \text{ mole} \\
 \text{No. of moles of Na}_2\text{S}_2\text{O}_3 \text{ in 1000g water} &= 3.528 \text{ mole} \\
 \text{Molality of Na}^+ \text{ ions} &= 2 \times 3.528 \text{ moles} && [\because \text{Na}_2\text{S}_2\text{O}_3 \equiv 2 \text{ Na}^+] \\
 &= \mathbf{7.056 \text{ m}} \\
 \text{and Molality of S}_2\text{O}_3^{2-} \text{ ions} &= 1 \times 3.528 \text{ moles} && [\because \text{Na}_2\text{S}_2\text{O}_3 \equiv \text{S}_2\text{O}_3^{2-}] \\
 &= \mathbf{3.528 \text{ m}}
 \end{aligned}$$

SOLVED PROBLEM 16. Calculate the molality of water in pure water.

SOLUTION :

$$\begin{aligned}
 \text{Mass of 1 litre of pure water} &= \text{Density} \times \text{volume} \\
 &= 1.0 \text{ g ml}^{-1} \times 1000 \text{ ml} \\
 &= 1000 \text{ g} \\
 \text{Molar mass of H}_2\text{O} &= 18 \text{ g mol}^{-1}
 \end{aligned}$$

$$\therefore \text{No. of moles of H}_2\text{O in 1000 g of pure water} = \frac{1000 \text{ g}}{18 \text{ g mol}^{-1}}$$

$$\text{Molality, } m = 55.55 \text{ m}$$

SOLVED PROBLEM 17. $8.0575 \times 10^{-2} \text{ kg}$ of Glauber's salt is dissolved in water to obtain 1 dm^3 of a solution of density 1077.2 kg m^{-3} . Calculate the molarity, molality and mole fraction of Na_2SO_4 in the solution.

SOLUTION :

$$\text{Mass of Glauber's salt, Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O dissolved} = 8.0575 \times 10^{-2} \text{ kg}$$

$$\text{Molar mass of Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} = 46 + 32 + 64 + 180 = 322 \text{ g mol}^{-1}$$

$$\begin{aligned} \text{Number of moles of Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} &= \frac{8.0575 \times 10^{-2}}{322 \times 10^{-3} \text{ kg mol}^{-1}} \\ &= 0.25 \text{ mole} \end{aligned}$$

$$\begin{aligned} \text{Mass of } 1 \text{ dm}^3 \text{ (1 lit.) solution of Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O} &= \text{Density} \times \text{volume} \\ &= 1077.2 \text{ kg m}^{-3} \times 10^{-3} \text{ m}^3 \\ &= 1.0772 \text{ kg} \end{aligned}$$

$$322 \text{ g of Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O contains Na}_2\text{SO}_4 = 142 \text{ g}$$

$$8.0575 \times 10^{-2} \text{ kg of Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O contains Na}_2\text{SO}_4 = \frac{142 \times 8.0575 \times 10^{-2} \text{ kg}}{322}$$

$$= 3.553 \times 10^{-2} \text{ kg}$$

$$\begin{aligned} \text{Mass of water in } 1 \text{ dm}^3 \text{ solution (1litre)} &= 1.0772 \text{ kg} - 3.553 \times 10^{-2} \text{ kg} \\ &= 1.04167 \text{ kg} \end{aligned}$$

(i) To calculate molarity of Na_2SO_4

Formula used

$$\begin{aligned} \text{Molarity, } M &= \frac{\text{No of moles of Na}_2\text{SO}_4}{\text{Vol. of solution in dm}^3 \text{ (litre)}} \\ &= \frac{0.25 \text{ mole}}{1 \text{ dm}^3} = 0.25 \text{ M} \end{aligned}$$

(ii) To calculate molality of Na_2SO_4

Formula used

$$\begin{aligned} \text{Molality, } m &= \frac{\text{No of moles of Na}_2\text{SO}_4}{\text{Mass of water in kg}} \\ &= \frac{0.25 \text{ mole}}{1.04167 \text{ kg}} = 0.2400 \text{ m} \end{aligned}$$

(iii) To calculate mole fraction of Na_2SO_4

Formula used

$$\begin{aligned} \text{Mole fraction of Na}_2\text{SO}_4, X_{\text{Na}_2\text{SO}_4} &= \frac{\text{No of moles of Na}_2\text{SO}_4}{\text{Total no. of moles}} \\ &= \frac{0.25 \text{ mole}}{\frac{1.04167 \times 10^3}{18} + 0.25 \text{ mole}} \\ &= \frac{0.25 \text{ mole}}{57.87 + 0.25 \text{ mole}} \\ &= \frac{0.25 \text{ mole}}{58.12 \text{ mole}} = 0.0043 \end{aligned}$$

ADDITIONAL PRACTICE PROBLEMS

1. A solution contains 100 g of NaCl and 900 g of water. Calculate the mole fraction of the components of the solution.
Answer. 0.0331 and 0.9669
2. Calculate the molarity of a solution containing 331g of HCl dissolved in sufficient water to make 2 dm³ of solution.
Answer. 4.534 M
3. Calculate the molality of a solution containing 100 g of H₂SO₄ dissolved in 2 kg of water.
Answer. 0.51 m
4. How many grams of Na₂CO₃ should be added to 2000 g of water in order to prepare 0.100 m solution of Na₂CO₃ ?
Answer. 21.2 g
5. What is the normality of a solution containing 28.0 g of KOH dissolved in sufficient water to make 400 ml of solution ?
Answer. 1.25 N
6. Calculate the molarity, molality and mole fraction of ethyl alcohol in a solution of total volume 172 ml obtained by adding 100 ml ethyl alcohol ($d = 0.789 \text{ g ml}^{-1}$) to 100 ml of water ($d = 1.0 \text{ g ml}^{-1}$)
Answer. 9.953 M ; 17.12 m ; 0.0299
7. Calculate the molality and mole fraction of the solute in a aqueous solution containing 5.0 g of urea in 250 g of water. (molecular mass of urea = 60)
Answer. 0.0833 m ; 0.00596
8. A solution has 20% water, 20% ethyl alcohol and 60% acetic acid by mass. Calculate the mole fraction of each component.
Answer. 0.437 ; 0.170 ; 0.393
9. Calculate the molarity and normality of a solution containing 5.3 g of Na₂CO₃ dissolved in 1000 ml solution.
Answer. 0.05 M ; 0.10 N
10. Calculate the molarity of the diluted solution obtained by diluting 1 litre of 12 M HCl to 20 litre.
Answer. 0.6 m
11. Water was added to 25.0 ml of 98 percent H₂SO₄, density 1.84 g ml⁻¹ to make 100 ml solution. Calculate the normality and molarity of the solution.
Answer. 9.2 N ; 4.6 M
12. A 6.90 M solution of KOH in water contains 30% by weight of KOH. Calculate the density of the solution.
Answer. 1.288 g ml⁻¹
13. Concentrated NH₄OH has a density of 0.90 g ml⁻¹ and is 28 percent by weight. What is its normality ?
Answer. 15 N
14. Calculate the molarity and molality of a solution of K₂CO₃ containing 22% of the salt by weight and has a density of 1.21 g ml⁻¹.
Answer. 1.93 M ; 2.04 m

15. What is molarity of Fe^{2+} ions in a solution containing 200 g of FeCl_3 per litre of solution ?
Answer. 1.574 M
16. 5 g of NaCl is dissolved in 1 kg of water. If the density of the solution is 0.997 g ml^{-1} , calculate the molarity, molality and mole fraction of the solute.
Answer. 0.085 M, 0.0847 m, 0.00153
17. How many kilograms of wet AlCl_3 containing 24% water are required to prepare 100 litres of 0.5 M solution.
Answer. 8.782 kg
18. A sugar syrup of weight 214.2 g contains 34.2 g of sugar ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$). Calculate (i) molal concentration and (ii) mole fraction of sugar in syrup.
Answer. (i) 0.556 m ; (ii) 0.0099
19. A water solution contains 8.0% sugar by weight and has a density of 1.03 g ml^{-1} . How many grams of sugar are there in 400 ml of the solution ?
Answer. 33.0 g
20. Calculate the amount of Na^+ and Cl^- ions in grams present in 500 ml of 1.5 M NaCl solution.
Answer. 17.3 g Na^+ and 26.6 g Cl^-
21. Calculate the number of molecules of sugar present in 1 ml of 10% sugar solution having density = 1.20 g ml^{-1} .
Answer. 2.1×10^{20}
22. The acid solution in a fully charged lead storage battery contains one-third of sulphuric acid by weight and has a density of 1.25 g ml^{-1} . Calculate the molarity and molality and mole fraction of the acid solution.
Answer. 4.21 M ; 5.02 m

15

Theory of Dilute Solutions

CHAPTER

KEY CONCEPTS AND EQUATIONS



COLLIGATIVE PROPERTIES

Certain properties of solutions which depend only on the concentration (number of particles) of solute particles are called colligative properties. These are independent of the size or nature of the particles. Colligative properties may be used to measure the concentration of solute. In this way, we can determine the molecular weight of the solute.

LOWERING OF VAPOUR PRESSURE - RAOULT'S LAW

When a non-volatile solute is dissolved in a solvent, the vapour pressure of the pure solution is lowered than that of pure solvent. This lowering of vapour pressure relative to the vapour pressure of the pure solvent is equal to the mole fraction of the solute in dilute solution. (Raoult's law) *i.e.*

$$\frac{p - p_s}{p} = \frac{n}{n + N}$$

where p is the vapour pressure of the pure solvent, p_s the vapour pressure of solution, n the number of moles of solute and N the number of moles of solvent.

DETERMINATION OF MOLECULAR MASS

If w is the mass of the solute of molecular mass m dissolved in W grams of solvent of molecular mass M , we can write :

$$\frac{p - p_s}{p} = \frac{\frac{w}{m}}{\frac{w}{m} + \frac{W}{M}}$$

For a very dilute solution w/m is very small and is negligible in the denominator, then we have

$$\frac{p - p_s}{p} = \frac{w/m}{W/M} = \frac{wM}{Wm}$$

From this we can calculate the molecular mass of the solute if other parameters are given.

BOILING POINT ELEVATION

The addition of non-volatile solute lowers the vapour pressure and the solution has to be heated to a higher temperature in order to make its vapour pressure equal to the atmospheric pressure. *i.e.*

Elevation in boiling point occurs. The elevation in boiling point, ΔT is given by

$$\Delta T_b = T - T_b$$

where T is the boiling point of the solution and T_b , the boiling point of pure solvent. The elevation in boiling point, ΔT is directly proportional to the relative lowering of vapour pressure, *i.e.*

$$\Delta T_b \propto \frac{p - p_s}{p}$$

From Raoult's law we can write

$$\Delta T_b \propto \frac{wM}{Wm} \quad \left[\because \frac{p - p_s}{p} = \frac{wM}{Wm} \right]$$

or

$$\Delta T_b = K_b \times \frac{w}{m} \times \frac{1}{W} \quad [\text{since } M \text{ is constant}]$$

where K_b is a constant called **Boiling point constant** or **Molal Elevation constant**. It is defined as the **boiling point elevation produced when 1 mole of the solute is dissolved in 1 kg (1000g) of the solvent**. If the mass of the solvent (W) is given in grams, it has to be converted into kilograms. Then we have

$$\Delta T_b = K_b \times \frac{w}{m} \times \frac{1}{W/1000}$$

or

$$\text{the molecular mass, } m = \frac{K_b \times 1000 \times w}{\Delta T_b \times W}$$

The molal elevation constant is characteristic of a particular solvent used. It can also be calculated by using the relation.

$$K_b = \frac{R T_b^2}{1000 \times L_v}$$

where R is gas constant, T_b , the boiling point of the solvent used and L_v the molar latent heat of vaporisation.

FREEZING POINT DEPRESSION

The addition of a non-volatile solute lowers the vapour pressure and the freezing point decreases. This difference of the freezing point of pure solvent and the solution is called depression in freezing point, denoted by ΔT_f . It is given by

$$\Delta T_f = T_f - T$$

where T_f is the freezing point of pure solvent and T , the freezing point of the solution. It is directly proportional to the relative lowering of vapour pressure *i.e.*

$$\Delta T_f \propto \frac{p - p_s}{p}$$

From Raoult's law we can write

$$\Delta T_f \propto \frac{wM}{Wm} \quad \left[\because \frac{p - p_s}{p} = \frac{wM}{Wm} \right]$$

or

$$\Delta T_f \propto \frac{w}{Wm} \quad [\text{since } M \text{ is constant}]$$

or

$$\begin{aligned} \Delta T_f &\propto \frac{w}{m} \times \frac{1}{W} \\ &= K_f \times \frac{w}{m} \times \frac{1}{W} \end{aligned}$$

where K_f is called the **Freezing point constant or Molal depression constant**. It is defined as the **freezing point depression produced when 1 mole of solute is dissolved in one kg (1000 g) of the solvent**. If the mass of solvent (W) is in grams, it has to be converted into kilograms, then we can write

$$\Delta T_f = K_f \times \frac{w}{m} \times \frac{1}{W/1000}$$

or molecular mass of solute, $m = \frac{K_f \times 1000 \times w}{\Delta T_f \times W}$

The molal depression constant is characteristic of a particular solvent used. It can also be calculated by using the relation.

$$K_f = \frac{R T_f^2}{1000 \times L_f}$$

COLLIGATIVE PROPERTIES OF ELECTROLYTES

The electrolytes ionise in solution and yield more than one particle per formula unit in the solution. Therefore, the colligative effect of an electrolyte is always greater than that of a non-electrolyte of the same molal concentration. To account for the effect of electrolytes, a factor known as van't Hoff factor, i , was introduced. **It is defined as ratio of the colligative effect produced by an electrolyte solution to corresponding effect for the same concentration of a non-electrolyte solution, i.e.**

$$i = \frac{\Delta T_f}{[\Delta T_f]_0} = \frac{\Delta T_b}{[\Delta T_b]_0} = \frac{\Delta p}{[\Delta p]_0}$$

where ΔT_f , ΔT_b and Δp are elevation in boiling point, depression in freezing point and lowering of vapour pressure for the electrolyte solution and $[\Delta T_f]_0$, $[\Delta T_b]_0$ and $[\Delta p]_0$ are corresponding colligative properties for non-electrolyte solution of the same molal concentrations.

The van't Hoff factor, i , can be calculated by using any colligative property *eg.*

$$\Delta T_b = \frac{i \times 1000 \times K_b \times w}{m \times W}$$

ABNORMAL MOLECULAR MASSES OF ELECTROLYTES

In case of electrolytes, which dissociate into ions, the experimental molecular mass will always be less than the theoretical value calculated from the formula. The van't Hoff factor, i , is also equal to the ratio of number of particles in solution to the number obtained assuming no ionisation, *i.e.*

$$i = \frac{\text{Actual number of particles}}{\text{Number of particles for no ionisation}}$$

The degree of dissociation is the fraction of a electrolyte which is dissociated into ions in aqueous solution. It is denoted by λ and is related to the van't Hoff factor by the relation

$$\lambda = \frac{i - 1}{v - 1}$$

where v is the no. of ions formed on complete dissociation of 1 mole of an electrolyte.

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. A Solution containing 10.0 g of a compound in 100 g of water lowers the vapour pressure from 17.5 mm of Hg to 17.41 mm of Hg at 20°C. Calculate the molecular mass of the compound.

SOLUTION :

Formula used

$$\frac{p - p_s}{p} = \frac{w \times M}{m \times W}$$

Quantities given

$$p = 17.5 \text{ mm of Hg}$$

$$w = 10 \text{ g}$$

Substitution of values

$$p_s = 17.41 \text{ mm of Hg}$$

$$W = 100 \text{ g}$$

$$w = 18 \text{ g}$$

$$\frac{17.5 \text{ mm} - 17.41 \text{ mm}}{17.5 \text{ mm}} = \frac{10 \text{ g} \times 18}{m \times 100 \text{ g}}$$

$$\text{or} \quad \frac{0.09}{17.5} = \frac{10 \times 18}{m \times 100}$$

$$\text{or} \quad m = \frac{10 \times 18 \times 17.5}{0.09 \times 100} = 350$$

SOLVED PROBLEM 2. 10 g of a non-volatile solute was dissolved in 100 g of acetone (molecular mass = 58) at 25 °C. The vapour pressure of the solution was found to be 192.5 mm Hg. Calculate the molecular mass of the solute. The vapour pressure of pure acetone at 25 °C is 195 mm Hg.

SOLUTION :**Formula used**

$$\frac{p - p_s}{p} = \frac{w \times M}{m \times W}$$

Quantities given

$$p = 195 \text{ mm Hg}$$

$$W = 100 \text{ g}$$

Substitution of values

$$p_s = 192.5 \text{ mm Hg}$$

$$M = 58$$

$$w = 10 \text{ g}$$

$$\frac{195 \text{ mm} - 192.5 \text{ mm}}{195 \text{ mm}} = \frac{10 \text{ g} \times 58}{100 \text{ g} \times m}$$

$$\text{or} \quad \frac{2.5}{195} = \frac{10 \times 58}{100 \times m}$$

$$\text{or} \quad m = \frac{10 \times 58 \times 195}{100 \times 2.5} = 452.4$$

SOLVED PROBLEM 3. Napthalene freezes at 80.1 °C. It has a molal depression constant 6.89 °C kg mol⁻¹. A solution of 3.2 g of sulphur in 100 g of napthalene freezes at a temperature 0.86 °C lower than pure napthalene. What is the molecular formula of sulphur in napthalene ?

SOLUTION :**Formula used**

$$\text{Molecular mass, } m = \frac{1000 \times K_f \times w}{\Delta T_f \times W}$$

Quantities given

$$K_f = 6.89 \text{ °C kg mol}^{-1}$$

$$W = 100 \text{ g}$$

Substitution of values

$$w = 3.2 \text{ g}$$

$$\Delta T_f = 0.86 \text{ °C}$$

$$m = \frac{1000 \times 6.89 \text{ °C kg mol}^{-1} \times 3.2 \text{ g}}{0.86 \text{ °C} \times 100 \text{ g}} = 256$$

$$\begin{aligned}\text{Number of sulphur atoms in naphthalene} &= \frac{\text{Calculated mol. mass}}{\text{Atomic mass of S}} \\ &= \frac{256}{32} = 8\end{aligned}$$

Thus, the molecular formula of sulphur in naphthalene is S_8 .

SOLVED PROBLEM 4. A Solution of urea in water has a freezing point of -0.400°C . Calculate the boiling point of the solution. ($K_f = 1.86$; $K_b = 0.51$)

SOLUTION :

Formula used

$$\text{molecular mass, } m = \frac{1000 \times K_f \times w}{\Delta T_f \times W} \quad \dots (i)$$

and

$$\text{molecular mass, } m = \frac{1000 \times K_b \times w}{\Delta T_b \times W} \quad \dots (ii)$$

Quantities given

$$\Delta T_f = 0.4^\circ\text{C}$$

$$K_f = 1.86^\circ\text{C}$$

$$K_b = 0.51^\circ\text{C}$$

Substitution in (i) and (ii) we have

$$m = \frac{1000 \times 1.86^\circ\text{C} \times w}{0.4^\circ\text{C} \times W} \quad \text{and} \quad m = \frac{1000 \times 0.51^\circ\text{C} \times w}{\Delta T_b \times W}$$

On equating we get

$$\frac{1000 \times 1.86^\circ\text{C} \times w}{0.4^\circ\text{C} \times W} = \frac{1000 \times 0.51 \times w}{\Delta T_b \times W}$$

$$\text{or} \quad 4650 = \frac{510}{\Delta T_b}$$

$$\text{or} \quad \Delta T_b = \frac{510}{4650} = 0.10968^\circ\text{C}$$

$$\begin{aligned}\therefore \text{Boiling point of the solution} &= \text{Boiling point of water} + \text{Elevation in boiling point} \\ &= 100^\circ\text{C} + 0.10968^\circ\text{C} \\ &= \mathbf{100.10968^\circ\text{C}}\end{aligned}$$

SOLVED PROBLEM 5. Boiling point of 2.5 m solution of glucose (mol mass = 180) in water was 101.3°C . Calculate the molal elevation constant of water.

SOLUTION :

Formula used

$$\Delta T_b = m \times K_b \quad \text{or} \quad K_b = \frac{\Delta T_b}{m}$$

Quantities given

$$\Delta T_b = 101.3^\circ\text{C} - 100^\circ\text{C} = 1.3^\circ\text{C}$$

$$m = 2.5$$

Substitution of values

$$K_b = \frac{1.3^\circ\text{C}}{2.5} = \mathbf{0.52^\circ\text{C}}$$

SOLVED PROBLEM 6. A solution of 8.585 g of sodium nitrate in 100 g of water freezes at -3.04°C . Calculate the molecular mass of sodium nitrate. (K_f for water = 1.86 K mol^{-1})

SOLUTION :**Formula used**

$$\text{molecular mass, } m = \frac{1000 \times K_f \times w}{\Delta T_f \times W}$$

Quantities given

$$K_f = 1.86 \text{ K mol}^{-1}$$

$$\Delta T_f = 3.04^\circ\text{C} = 3.04 \text{ K} \quad w = 8.585 \text{ g} \quad W = 100 \text{ g}$$

Substitution of values

$$\begin{aligned} m &= \frac{1000 \times 1.86 \text{ K mol}^{-1} \times 8.585 \text{ g}}{3.04 \text{ K} \times 100 \text{ g}} \\ &= \mathbf{52.52} \end{aligned}$$

SOLVED PROBLEM 7. A 0.1 molar solution of urea at the room temperature freezes at -0.25°C at normal pressure. What would be the approximate freezing point of 0.1 molal aqueous solution of aluminium chloride at room temperature assuming complete ionisation ?

SOLUTION :**Formula used**

$$\Delta T_f = K_f \times m \quad \text{or} \quad K_f = \frac{\Delta T_f}{m}$$

Quantities given

$$\Delta T_f = 0.25^\circ\text{C}$$

$$m = 0.1$$

Substitution of values

$$K_f = \frac{0.25^\circ\text{C}}{0.1} = 2.5^\circ\text{C}$$

Now, for AlCl_3

$$\begin{aligned} \Delta T_f &= K_f \times m \\ &= 2.5^\circ\text{C} \times 0.1 \\ &= \mathbf{0.25^\circ\text{C}} \end{aligned}$$

SOLVED PROBLEM 8. The values of molal elevation constant and molal depression constant for water are 0.52 and $1.86^\circ\text{C kg mol}^{-1}$ respectively. If the elevation in boiling point by dissolving a solute in water is $+0.2^\circ\text{C}$, what will be the depression in freezing point of this solution ?

SOLUTION :**Formula used**

$$\Delta T_b = K_b \times m \quad \text{and} \quad \Delta T_f = K_f \times m$$

or

$$\frac{\Delta T_b}{\Delta T_f} = \frac{K_b}{K_f}$$

Quantities given

$$\Delta T_b = 0.2^\circ\text{C}$$

$$K_b = 0.52^\circ\text{C kg mol}^{-1}$$

$$K_f = 1.86^\circ\text{C kg mol}^{-1}$$

Substitution of values

$$\frac{0.2^\circ\text{C}}{\Delta T_f} = \frac{0.52^\circ\text{C kg mol}^{-1}}{1.86^\circ\text{C kg mol}^{-1}}$$

or

$$\begin{aligned} \Delta T_f &= \frac{1.86 \times 0.2^\circ\text{C}}{0.52} \\ &= \mathbf{0.715^\circ\text{C}} \end{aligned}$$

SOLVED PROBLEM 9. 1.065 g of an organic solute dissolved in 30.14 g of diethyl ether raises the boiling point by 0.296°C . The molal elevation constant of ether is 2.11. Calculate the molecular mass of the solute.

SOLUTION :**Formula used**

$$m = \frac{1000 \times K_b \times w}{\Delta T_b \times W}$$

Quantities given

$$K_b = 2.11^\circ\text{C}$$

$$w = 1.065 \text{ g}$$

$$\Delta T_b = 0.296^\circ\text{C}$$

$$W = 30.14 \text{ g}$$

Substitution of values

$$\begin{aligned} m &= \frac{1000 \times 2.11^\circ\text{C} \times 1.065 \text{ g}}{0.296^\circ\text{C} \times 30.14 \text{ g}} \\ &= \mathbf{251.88} \end{aligned}$$

SOLVED PROBLEM 10. A 0.5 percent solution of potassium chloride was found to freeze at -0.24°C . Calculate the degree of dissociation of potassium chloride. (Molal depression constant for water $= 1.80^\circ\text{C}$)

SOLUTION :**(i) To calculate the molecular mass of KCl****Formula used**

$$m = \frac{1000 \times K_f \times w}{\Delta T_f \times W}$$

Quantities given

$$K_b = 1.80^\circ\text{C}$$

$$\Delta T_f = 0.24^\circ\text{C}$$

$$w = 5 \text{ g}$$

$$W = 99.5 \text{ g}$$

Substitution of values

$$\begin{aligned} m &= \frac{1000 \times 1.80^\circ\text{C} \times 0.5 \text{ g}}{0.24^\circ\text{C} \times 99.5 \text{ g}} \\ &= \mathbf{37.69} \end{aligned}$$

(ii) To calculate the degree of dissociation of KCl

$$\text{The observed molecular mass} = 37.69$$

$$\text{and the normal molecular mass} = 38 + 35.5 = 73.5$$

$$\begin{aligned} \text{van't Hoff factor, } i &= \frac{\text{Normal molecular mass}}{\text{observed molecular mass}} \\ &= \frac{73.5}{37.69} = 1.950 \end{aligned}$$

The degree of dissociation is related to van't Hoff factor by the relation

$$i = 1 + \alpha$$

$$\text{or } 1.950 = 1 + \alpha$$

$$\text{or } \alpha = \mathbf{0.95 \text{ or } 95\%}$$

SOLVED PROBLEM 11. 10 g of a substance is dissolved in 100 g of water at 25°C . The vapour pressure of water is lowered from 17.5 mm to 17.2 mm. Calculate the molecular mass of the solute.

SOLUTION :**Formula used**

$$\frac{p - p_s}{p} = \frac{w \times M}{m \times W}$$

Quantities given

$$p = 17.5 \text{ mm}$$

$$W = 100 \text{ g}$$

$$p_s = 17.2 \text{ mm}$$

$$M = 18$$

$$w = 10 \text{ g}$$

Substitution of values

$$\begin{aligned} \frac{17.5 \text{ mm} - 17.2 \text{ mm}}{17.5 \text{ mm}} &= \frac{10 \text{ g} \times 18}{m \times 100 \text{ g}} \\ \text{or} \quad \frac{0.3 \text{ mm}}{17.5 \text{ mm}} &= \frac{10 \times 18}{m \times 100 \text{ g}} \\ \text{or} \quad m &= \frac{10 \times 18 \times 17.5}{100 \times 0.3} \\ &= \mathbf{105} \end{aligned}$$

SOLVED PROBLEM 12. 20 g of a non-volatile substance (mol mass = 60) was dissolved in 100 g of water. Calculate the vapour pressure of the solution at 100 °C.

SOLUTION :

Formula used

$$\frac{p - p_s}{p} = \frac{w \times M}{m \times W}$$

Quantities given

$$p = 760 \text{ mm}$$

$$m = 60$$

$$w = 20 \text{ g}$$

$$M = 18$$

$$W = 100 \text{ g}$$

Substitution of values

$$\begin{aligned} \frac{760 \text{ mm} - p_s}{760 \text{ mm}} &= \frac{20 \text{ g} \times 18}{60 \times 100 \text{ g}} \\ \text{or} \quad 760 \text{ mm} - p &= \frac{760 \text{ mm} \times 20 \times 18}{60 \times 100} \\ \text{or} \quad 760 \text{ mm} - p &= 45.6 \text{ mm} \\ p_s &= 760 \text{ mm} - 45.6 \text{ mm} \\ &= \mathbf{714.4 \text{ mm}} \end{aligned}$$

SOLVED PROBLEM 13. The molecular mass of a water soluble non-electrolyte is 58. Compute the boiling point of a solution containing 24 g of the solute and 600 g of water at atmospheric pressure. (K_{1000} of water = 0.573)

SOLUTION :

Formula used

$$\Delta T_b = \frac{1000 \times K_b \times w}{m \times W}$$

Quantities given

$$K_b = 0.573 ^\circ\text{C}$$

$$w = 24 \text{ g}$$

$$W = 600 \text{ g}$$

$$m = 58$$

Substitution of values

$$\begin{aligned} \Delta T_b &= \frac{1000 \times 0.573 ^\circ\text{C} \times 24 \text{ g}}{58 \times 600 \text{ g}} \\ &= 0.395 ^\circ\text{C} \end{aligned}$$

$$\begin{aligned} \text{Thus} \quad \text{the boiling point of solution} &= \text{Boiling point of water} + \Delta T_b \\ &= 100 ^\circ\text{C} + 0.395 ^\circ\text{C} \\ &= \mathbf{100.395 ^\circ\text{C}} \end{aligned}$$

SOLVED PROBLEM 14. When a certain amount of solute is added to 100 g of water at 25 °C, the vapour pressure reduces to one half of that for pure water. The vapour pressure of water is 23.76 mm Hg. Find out the amount of salt added.

SOLUTION :**Formula used**

$$\frac{p - p_s}{p} = \frac{w \times M}{m \times W}$$

Quantities given

$$p = 23.76 \text{ mm}$$

$$W = 100 \text{ g}$$

$$P_s = \frac{1}{2} p = \frac{1}{2} \times 23.76 \text{ mm} = 11.88 \text{ mm}$$

$$M = 18$$

Substitution of values

$$\frac{23.76 \text{ mm} - 11.88 \text{ mm}}{23.76 \text{ mm}} = \frac{w}{m} \times \frac{18}{100}$$

or

$$\frac{11.88 \text{ mm}}{23.76 \text{ mm}} = \frac{w}{m} \times \frac{18}{100}$$

or

$$\begin{aligned} \frac{w}{m} &= \frac{1}{2} \times \frac{100}{18} \\ &= \mathbf{2.78 \text{ mole}} \end{aligned}$$

SOLVED PROBLEM 15. $0.3 \times 10^{-3} \text{ kg}$ of camphor (molar mass $154.5 \times 10^{-3} \text{ kg mol}^{-1}$) when added to $25.2 \times 10^{-3} \text{ kg}$ of chloroform raised the boiling point of the solvent by 0.299 K . Calculate the molecular elevation constant of chloroform.

SOLUTION :**Formula used**

$$m = \frac{K_b \times 1000 \times w}{\Delta T_b \times W}$$

or

$$K_b = \frac{m \times \Delta T_b \times W}{1000 \times w}$$

Quantities given

$$m = 154.5 \text{ g mol}^{-1} = 154.5 \times 10^{-3} \text{ kg mol}^{-1}$$

$$W = 25.2 \times 10^{-3} \text{ kg}$$

$$w = 0.3 \times 10^{-3} \text{ kg}$$

$$\Delta T_b = 0.299 \text{ K}$$

Substitution of values

$$\begin{aligned} K_b &= \frac{154.5 \times 10^{-3} \text{ kg mol}^{-1} \times 0.299 \text{ K} \times 25.2 \times 10^{-3} \text{ kg}}{1000 \times 0.3 \times 10^{-3} \text{ kg}} \\ &= \mathbf{3.88 \times 10^{-3} \text{ K kg mol}^{-1}} \end{aligned}$$

SOLVED PROBLEM 16. When 0.946 g of sugar is dissolved in 150 g of water, the resulting solution is observed to have a freezing point of 0.0651°C . What is the molecular mass of sugar ? (K_f for water is 1.86°C).

SOLUTION :**Formula used**

$$\text{molecular mass, } m = \frac{1000 \times K_f \times w}{\Delta T_f \times W}$$

Quantities given

$$K_f = 1.86^\circ \text{C}$$

$$w = 0.946 \text{ g}$$

$$\Delta T_f = 0.0651^\circ \text{C}$$

$$W = 150 \text{ g}$$

Substitution of values

$$\begin{aligned} m &= \frac{1000 \times 1.86^\circ \text{C} \times 0.946 \text{ g}}{0.0651^\circ \text{C} \times 150 \text{ g}} \\ &= \mathbf{180} \end{aligned}$$

SOLVED PROBLEM 16. An immiscible liquid system composed of water and an organic liquid boils at 95°C when the barometer reads 740 mm. The vapour pressure of pure liquid at this temperature is 63 mm. The distillate contains 55% of the weight of the organic compound. Calculate the molecular mass of the organic compound.

SOLUTION :

Formula used

$$\frac{w_1}{w_2} = \frac{p_1}{p_2} \times \frac{M_1}{M_2}$$

Quantities given

$$w_1 = 45$$

$$w_2 = 55$$

$$M_1 = 18$$

$$p_1 \text{ (water)} = \text{Vap. pressure of mixture} - \text{Vap. pressure of liquid} = 740 \text{ mm} - 63 \text{ mm} = 677 \text{ mm}$$

Substitution of values

$$\frac{45}{55} = \frac{677 \text{ mm}}{63 \text{ mm}} \times \frac{18}{M_2}$$

or

$$\begin{aligned} M_2 &= \frac{677 \times 18 \times 55}{63 \times 45} \\ &= \mathbf{236} \end{aligned}$$

SOLVED PROBLEM 17. A solution containing 7.5 g of urea (mol mass 60) in one kg of water freezes at the same temperature as another solution containing 15 g of solute *S* in the same amount of water. Calculate the molecular mass of *S*.

SOLUTION :

Formula used

$$\Delta T_f = \frac{1000 \times K_f \times w}{m \times W}$$

(i) For urea

Quantities given

$$w = 7.5 \text{ g}$$

$$m = 60$$

$$W = 1 \text{ kg} = 1000 \text{ g}$$

Substitution of values

$$\Delta T_f = \frac{1000 \times K_f \times 7.5 \text{ g}}{60 \times 1000 \text{ g}} = 0.125 K_f$$

(ii) For solute S

Quantities given

$$w = 15 \text{ g}$$

$$W = 1000 \text{ g}$$

Substitution of values

$$\Delta T_f = \frac{1000 \times K_f \times 15 \text{ g}}{m \times 1000 \text{ g}} = 15 \frac{K_f}{m}$$

Since ΔT_f is the same in both cases, we have

$$0.125 K_f = 15 \frac{K_f}{m}$$

or

$$\begin{aligned} m &= \frac{15}{0.125} \\ &= \mathbf{120} \end{aligned}$$

SOLVED PROBLEM 18. A solution containing 12.5 g of unknown solute in 170 g water gave a boiling point elevation of 0.63 K. Calculate the molar mass of the solute ($K_b = 0.52 \text{ K}$).

SOLUTION :**Formula used**

$$m = \frac{1000 \times K_b \times w}{\Delta T_b \times W}$$

Quantities given

$$K_b = 0.52 \text{ K}$$

$$w = 12.5 \text{ g}$$

$$W = 170 \text{ g}$$

$$\Delta T_b = 0.63 \text{ K}$$

Substitution of values

$$\begin{aligned} m &= \frac{1000 \times 0.52 \text{ K} \times 12.5 \text{ g}}{0.63 \text{ K} \times 170 \text{ g}} \\ &= \mathbf{60.69} \end{aligned}$$

SOLVED PROBLEM 19. The relative molar mass of an ionic compound is 58.5. If the experimentally observed molar mass is 30, calculate van't Hoff factor.

SOLUTION :**Formula used**

$$\text{van't Hoff factor, } i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}$$

Quantities given

$$\text{Normal molecular mass} = 58.5$$

$$\text{Observed molecular mass} = 30$$

Substitution of values

$$\begin{aligned} \text{van't Hoff factor, } i &= \frac{58.5}{30} \\ &= \mathbf{1.95} \end{aligned}$$

SOLVED PROBLEM 20. 1.8 of glucose (mol mass 180) is dissolved in 100 grams of water. Calculate the freezing and boiling point of the solution. Molal freezing point constant of water = 1.86. Molal boiling point constant of water = 0.513

SOLUTION :**(i) To calculate the freezing point of the solution****Formula used**

$$\Delta T_f = \frac{1000 \times K_f \times w}{m \times W}$$

Quantities given

$$K_f = 1.86^\circ\text{C}$$

$$w = 1.8 \text{ g}$$

$$m = 180$$

$$W = 100 \text{ g}$$

Substitution of values

$$\begin{aligned} \Delta T_f &= \frac{1000 \times 1.86^\circ\text{C} \times 1.8 \text{ g}}{180 \times 100 \text{ g}} \\ &= 0.186^\circ\text{C} \end{aligned}$$

$$\begin{aligned} \therefore \text{ The freezing point of solution} &= 0^\circ\text{C} - \Delta T_f \\ &= 0^\circ\text{C} - 0.186^\circ\text{C} \\ &= -0.186^\circ\text{C} \end{aligned}$$

(ii) To calculate the boiling point of the solution**Formula used**

$$\Delta T_b = \frac{1000 \times K_b \times w}{m \times W}$$

Quantities given

$$K_b = 0.513^\circ\text{C} \quad w = 1.8 \text{ g} \quad m = 180 \quad W = 100 \text{ g}$$

Substitution of values

$$\begin{aligned} \Delta T_b &= \frac{1000 \times 0.513^\circ\text{C} \times 1.8 \text{ g}}{180 \times 100 \text{ g}} \\ &= 0.0513^\circ\text{C} \\ \therefore \text{ The boiling point of solution} &= 100^\circ\text{C} + \Delta T_b \\ &= 100 + 0.0513^\circ\text{C} \\ &= \mathbf{100.0513^\circ\text{C}} \end{aligned}$$

SOLVED PROBLEM 21. Calculate the value of K_b for water, given that pure water boils at 100°C and latent heat of its vaporisation is 540 cal g^{-1} .

SOLUTION :**Formula used**

$$K_b = \frac{R \times T_b^2}{1000 \times L_v}$$

Quantities given

$$R = 1.99 \text{ cal} \quad T_b = 100 + 273 = 373 \text{ K} \quad L_v = 540 \text{ cal g}^{-1}$$

Substitution of values

$$\begin{aligned} K_b &= \frac{1.99 \text{ cal} \times (373 \text{ K})^2}{1000 \times 540 \text{ cal}} \\ &= \mathbf{0.512 \text{ K}} \end{aligned}$$

SOLVED PROBLEM 22. The molal elevation constant K_b and the boiling point for carbon tetrachloride are 5.02 deg/molal and 76.80°C respectively. Calculate boiling point of 1.0 molal solution of naphthalene in carbon tetrachloride.

SOLUTION :**Formula used**

$$\Delta T_b = K_b \times m$$

Quantities given

$$K_b = 5.02^\circ\text{C/molal} \quad m = 1.0 \text{ (for naphthalene)}$$

Substitution of values

$$\begin{aligned} \Delta T_b &= 5.02^\circ\text{C/molal} \times 1.0 \text{ molal} \\ &= 5.02^\circ\text{C} \\ \therefore \text{ The boiling point of 1 molal solution of naphthalene in chloroform} &= \text{boiling point of chloroform} + \Delta T_b \\ &= 76.8^\circ\text{C} + 5.02^\circ\text{C} \\ &= \mathbf{81.82^\circ\text{C}} \end{aligned}$$

SOLVED PROBLEM 23. 8.0 g of solute dissolved in 100 g of water boils at 100.255°C . Determine the molecular mass of the solute. (K_b for water 0.51)

SOLUTION :**Formula used**

$$m = \frac{1000 \times K_b \times w}{\Delta T_b \times W}$$

Quantities given

$$K_b = 0.51^\circ\text{C}$$

$$w = 8.0\text{ g}$$

$$\Delta T_b = 0.255^\circ\text{C}$$

Substitution of values

$$\begin{aligned} m &= \frac{1000 \times 0.51^\circ\text{C} \times 8.0\text{ g}}{0.255^\circ\text{C} \times 100\text{ g}} \\ &= \mathbf{160} \end{aligned}$$

SOLVED PROBLEM 24. A solution containing 5.0 g of KCl per litre of water boils at 100.065°C at 760 mm pressure. Determine the degree of dissociation of KCl. (K_b for water = 0.54°C)

SOLUTION :**(i) To calculate the molecular mass of KCl.****Formula used**

$$m = \frac{1000 \times K_b \times w}{\Delta T_b \times W}$$

Quantities given

$$m = 5.0\text{ g}$$

$$K_b = 0.54^\circ\text{C}$$

$$\Delta T_b = 0.065^\circ\text{C}$$

$$W = 1000\text{ g}$$

Substitution of values

$$\begin{aligned} m &= \frac{1000 \times 0.54^\circ\text{C} \times 5.0\text{ g}}{0.065^\circ\text{C} \times 1000\text{ g}} \\ &= 41.53 \end{aligned}$$

(ii) To calculate the degree of dissociation**Formula used**

$$\begin{aligned} i &= \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}} \\ &= \frac{74.5}{41.53} = 1.7939 \end{aligned}$$

and

$$i = 1 + \alpha$$

or

$$1.7939 = 1 + \alpha$$

or

$$\alpha = \mathbf{0.7959 \text{ or } 79.59\%}$$

SOLVED PROBLEM 25. The boiling point of a solution containing 0.20 g of non-volatile substance X in 20 g of solvent is 0.17 higher than that of pure solvent. Calculate the molecular mass of X. Boiling point elevation constant of solvent per kg is 2.16 K.

SOLUTION :**Formula used**

$$m = \frac{1000 \times K_b \times w}{\Delta T_b \times W}$$

Quantities given

$$K_b = 2.16\text{ K}$$

$$w = 0.20\text{ g}$$

$$\Delta T_b = 0.17\text{ K}$$

$$W = 20\text{ g}$$

Substitution of values

$$\begin{aligned} m &= \frac{1000 \times 2.16\text{ K} \times 0.2\text{ g}}{0.17\text{ K} \times 20\text{ g}} \\ &= \mathbf{127} \end{aligned}$$

SOLVED PROBLEM 26. Molal elevation constant of Chloroform is 3.63 kg mol^{-1} . A solution of same organic solute boils at 0.15 K higher than Chloroform. What is the molality of the solution ?

SOLUTION :**Formula used**

$$\Delta T_b = K_b \times m \quad \text{or} \quad m = \frac{\Delta T_b}{K_b}$$

Quantities given

$$\Delta T_b = 0.15 \text{ K}$$

$$K_b = 3.63 \text{ K kg mol}^{-1}$$

Substitution of values

$$\begin{aligned} m &= \frac{0.15 \text{ K}}{3.63 \text{ K kg mol}^{-1}} \\ &= \mathbf{0.0413 \text{ m kg}^{-1}} \end{aligned}$$

SOLVED PROBLEM 27. The molal depression constant for benzene is 5.12 K mol^{-1} . A solution containing 1g solute per 100 g benzene freezes at 5.1°C . What is the molar mass of the solute? (Freezing point of pure benzene is 5.5°C)

SOLUTION :**Formula used**

$$m = \frac{1000 \times K_f \times w}{\Delta T_f \times W}$$

Quantities given

$$K_f = 5.12 \text{ K}$$

$$w = 1 \text{ g}$$

$$W = 100 \text{ g}$$

$$\Delta T_f = 5.5^\circ\text{C} - 5.1^\circ\text{C} = 0.4^\circ\text{C} = 0.4 \text{ K}$$

Substitution of values

$$\begin{aligned} m &= \frac{1000 \times 5.12 \text{ K} \times 1 \text{ g}}{0.4 \text{ K} \times 100 \text{ g}} \\ &= \mathbf{128} \end{aligned}$$

SOLVED PROBLEM 28. The vapour of pure benzene at a certain temperature is 640 mm Hg. A non-volatile solid weighing 2.175 g is added to 39.0 g of benzene. The vapour pressure of the solution is 600 mm Hg. What is the molecular weight of the solid substance ?

SOLUTION :**Formula used**

$$\frac{p - p_s}{p} = \frac{\frac{w}{m}}{\frac{w}{m} + \frac{W}{M}}$$

Quantities given

$$p = 640 \text{ mm}$$

$$p_s = 600 \text{ mm}$$

$$w = 2.175 \text{ g}$$

$$W = 39.0 \text{ g}$$

$$M = 78$$

Substitution of values

$$\begin{aligned} \frac{640 - 600 \text{ mm}}{640 \text{ mm}} &= \frac{\frac{2.175 \text{ g}}{m}}{\frac{2.175 \text{ g}}{m} + \frac{39 \text{ g}}{78}} \\ \frac{40 \text{ mm}}{640 \text{ mm}} &= \frac{2.175}{2.175 + 0.5 m} \end{aligned}$$

$$\begin{aligned} \text{or} \quad 2.175 + 0.5m &= \frac{2.175 \times 640}{40} \\ \text{or} \quad 0.5m &= 34.8 - 2.175 \\ \text{or} \quad m &= \mathbf{65.25} \end{aligned}$$

SOLVED PROBLEM 29. 2.0 g of benzoic acid dissolved in 25 g of benzene shows a depression in freezing point equal to 1.62 K. Molal depression constant K_f of benzene is $4.9 \text{ K kg mol}^{-1}$. What is the percentage association of the acid ?

SOLUTION :

(i) To calculate the molecular mass of benzoic acid

Formula used

$$m = \frac{1000 \times K_f \times w}{\Delta T_f \times W}$$

Quantities given

$$K_f = 4.9 \text{ K kg mol}^{-1} \quad w = 2 \text{ g} \quad \Delta T_f = 1.62 \text{ K} \quad W = 25 \text{ g}$$

Substitution of values

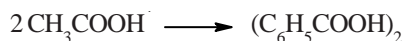
$$\begin{aligned} m &= \frac{1000 \times 4.9 \text{ K kg mol}^{-1} \times 2 \text{ g}}{1.62 \text{ K} \times 25 \text{ g}} \\ &= \mathbf{241.975} \end{aligned}$$

(ii) To calculate the degree of association of benzoic acid

$$\text{observed mol. mass of benzoic acid} = 241.975$$

$$\text{normal mol. mass of benzoic acid} = 122$$

$$\begin{aligned} \text{van't Hoff factor, } i &= \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}} \\ &= \frac{122}{241.975} = 0.504 \end{aligned}$$



Degree of association x is related to van't Hoff factor by the relation

$$i = 1 - \frac{x}{2}$$

$$\text{or} \quad 0.504 = 1 - \frac{x}{2}$$

$$\text{or} \quad 1.008 = 2 - x$$

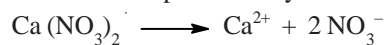
$$\begin{aligned} \text{or} \quad x &= 2 - 1.008 \\ &= \mathbf{0.992 \text{ or } 99.2\%} \end{aligned}$$

SOLVED PROBLEM 30. The degree of dissociation of Calcium nitrate in dilute aqueous solution containing 7.0 g of the salt per 100 g of water at 100°C is 70%. If the vapour pressure of water at 100°C is 760 mm. Calculate the vapour pressure of the solution.

SOLUTION :

(i) To calculate the number of moles of $\text{Ca}(\text{NO}_3)_2$ and H_2O

The dissociation of Calcium nitrate is represented by



$$\begin{array}{ccc} \text{Initial Conc.} & 1 & 0 \quad 0 \end{array}$$

$$\begin{array}{ccc} \text{Equilibrium Conc.} & 1 - 0.7 & 0.7 \quad 2 \times 0.7 \end{array}$$

$$\begin{aligned} \text{Total number of moles of equilibrium} &= (1 - 0.7) + 0.7 + 2 \times 0.7 \\ &= \mathbf{2.4} \end{aligned}$$

Number of moles at equilibrium when the conc. of $\text{Ca}(\text{NO}_3)_2$ is 7.0 g

$$= \frac{2.4 \times 7 \text{ g}}{164 \text{ g mol}^{-1}} = 0.1024 \text{ mole}$$

$$\text{Number of moles of water in 100 g} = \frac{100 \text{ g}}{18 \text{ g mol}^{-1}} = 5.55 \text{ moles}$$

(ii) To calculate the vapour pressure of the solution

Formula used

$$\frac{p - p_s}{p} = \frac{n}{n + N}$$

Quantities given

$$p = 760 \text{ mm}$$

$$n = 0.1024 \text{ mole}$$

$$N = 5.55 \text{ moles}$$

Substitution of values

$$\frac{760 \text{ mm} - p_s}{760 \text{ mm}} = \frac{0.1024 \text{ mole}}{0.1024 \text{ mole} + 5.55 \text{ mole}}$$

or

$$760 \text{ mm} - p_s = \frac{0.1024 \times 760 \text{ mm}}{5.6524}$$

or

$$760 \text{ mm} - p_s = 13.76 \text{ mm}$$

or

$$p_s = 760 \text{ mm} - 13.76 \text{ mm} \\ = \mathbf{746.24 \text{ mm}}$$

SOLVED PROBLEM 31. Addition of 0.643 g of a compound to 50 ml of benzene (density 0.879 g ml⁻¹) lowers the freezing point from 5.51 °C to 5.03 °C. If K_f for benzene is 5.12 K kg mol⁻¹, calculate the molar mass of the compound.

SOLUTION :

Formula used

$$m = \frac{1000 \times K_f \times w}{\Delta T_f \times W}$$

Quantities given

$$K_f = 5.12 \text{ K kg mol}^{-1}$$

$$\Delta T_f = 5.51^\circ\text{C} - 5.03^\circ\text{C} = 0.48^\circ\text{C} = 0.48 \text{ K}$$

$$w = 0.643 \text{ g}$$

$$W = 50 \text{ ml} \times 0.879 \text{ g ml}^{-1} = 43.95 \text{ g}$$

Substitution of values

$$m = \frac{1000 \times 5.12 \text{ K kg mol}^{-1} \times 0.643 \text{ g}}{0.48 \text{ K} \times 43.95 \text{ g}} \\ = \mathbf{156.056}$$

SOLVED PROBLEM 32. In a cold climate water gets frozen causing damage to the radiator of a car. Ethylene glycol is used as an antifreezing agent. Calculate the amount of ethylene glycol to be added to 4 kg of water to prevent it from freezing at -6 °C. (K_f for water = 1.85 K kg mol⁻¹)

SOLUTION :

Formula used

$$m = \frac{1000 \times K_f \times w}{\Delta T_f \times W}$$

Quantities given

$$K_f = 1.85 \text{ K kg mol}^{-1}$$

$$\Delta T_f = 6^\circ\text{C} = 6 \text{ K}$$

$$m \text{ of ethylene glycol [OHCH}_2\text{ - CH}_2\text{OH]} = 62$$

$$W = 4 \text{ kg} = 4 \times 10^3 \text{ g}$$

Substitution of values

$$62 = \frac{1000 \times 1.85 \text{ K kg mol}^{-1} \times w}{6 \text{ K} \times 4 \times 10^3 \text{ g}}$$

or

$$w = \frac{62 \times 6 \times 4 \times 10^3 \text{ g}}{1000 \times 1.85} = \mathbf{804.324 \text{ g}}$$

SOLVED PROBLEM 33. What mass of the non-volatile solute, urea, ($\text{NH}_2 \text{ CO NH}_2$) needs to be dissolved in 100 g of water in order to decrease the vapour pressure of water by 25%? What will be the molality of the solution?

SOLUTION :**Formula used**

$$\frac{p - p_s}{p} = \frac{\frac{w}{m}}{\frac{w}{m} + \frac{W}{M}}$$

Quantities given

$$p = p \text{ mm (say)}$$

$$m = 60$$

$$p_s = 75\% \text{ of } p \text{ mm} = \frac{3p}{4} \text{ mm}$$

$$W = 100 \text{ g} \quad M = 18$$

Substitution of values

$$\frac{p - \frac{3}{4} p}{p} = \frac{\frac{w}{60}}{\frac{w}{60} + \frac{100}{18}}$$

$$4 \times \frac{w}{60} = \frac{w}{60} + 5.55$$

or

$$\frac{4w}{60} - \frac{w}{60} = 5.55$$

or

$$\frac{3w}{60} = 5.55$$

or

$$w = \frac{60 \times 5.55}{3} = \mathbf{111 \text{ g}}$$

or

$$\begin{aligned} \text{Molality} &= \frac{\text{moles of solute}}{\text{mass of solvent in kg}} \\ &= \frac{111 \text{ g}}{60 \text{ g mol}^{-1} \times 100 \times 10^{-3} \text{ kg}} \\ &= \mathbf{18.50 \text{ m}} \end{aligned}$$

SOLVED PROBLEM 34. The freezing point of a solution containing 0.2 g of acetic acid in 20.0 g of benzene is lowered by 0.45°C . Calculate the degree of association of acetic acid in benzene. (K_f for benzene is $5.12 \text{ K mol}^{-1} \text{ kg}$)

SOLUTION :**(i) To calculate the molecular mass of acetic acid****Formula used**

$$m = \frac{1000 \times K_f \times w}{\Delta T_f \times m}$$

Quantities given

$$K_f = 5.12 \text{ K kg mol}^{-1}$$

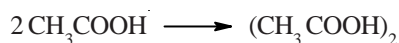
$$w = 0.2 \text{ g}$$

$$\Delta T = 0.45 \text{ K}$$

$$W = 20.0 \text{ g}$$

Substitution of values

$$\begin{aligned} m &= \frac{1000 \times 5.12 \text{ K kg mol}^{-1} \times 0.2 \text{ g}}{0.45 \text{ K} \times 20.0 \text{ g}} \\ &= 113.778 \end{aligned}$$

(ii) To calculate the degree of association of acetic acid

$$\begin{aligned} \text{The van't Hoff factor, } i &= \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}} \\ &= \frac{60}{113.378} = 0.527 \end{aligned}$$

Let the degree of association of acetic acid be = x

$$\text{and van't Hoff factor, } i = 1 - \frac{x}{2}$$

$$\text{or } 0.527 = 1 - \frac{x}{2}$$

$$\begin{aligned} \text{or } x &= 2 - 2 \times 0.527 \\ &= \mathbf{0.946 \text{ or } 94.6 \%} \end{aligned}$$

SOLVED PROBLEM 35. Calculate the amount of ice that will separate out on cooling a solution containing 50 g of ethylene glycol in 200 g of water to 9.3°C . (K_f for water = $1.86 \text{ K kg mol}^{-1}$)

SOLUTION :**Formula used**

$$m = \frac{1000 \times K_f \times w}{\Delta T_f \times W}$$

$$\text{or } w = \frac{1000 \times K_f \times m}{\Delta T_f \times W}$$

Quantities given

$$K_f = 1.86 \text{ K kg mol}^{-1}$$

$$w = 50 \text{ g}$$

$$\text{molecular mass, } m, \text{ of glycol (HOCH}_2\text{—CH}_2\text{OH)} = 62$$

$$\Delta T_f = 9.3 \text{ K}$$

Substitution of values

$$\begin{aligned} W &= \frac{1000 \times 1.86 \text{ K kg mol}^{-1} \times 50 \text{ g}}{9.3 \text{ K} \times 62} \\ &= 161.29 \text{ g} \end{aligned}$$

$$\begin{aligned} \text{Amt. of ice separated from 200 g water} &= 200 \text{ g} - 161.29 \text{ g} \\ &= \mathbf{38.71 \text{ g}} \end{aligned}$$

ADDITIONAL PRACTICE PROBLEMS

- Calculate the freezing point of a one molar aqueous solution (density = 1.04 g ml^{-1}) of KCl. K_f for water is $1.86 \text{ K kg mol}^{-1}$ (Atomic mass K = 39, Cl = 35.5)
Answer. 269.15 K
- Calculate the boiling point of one molar aqueous solution (density = 1.04 g ml^{-1}) of potassium Chloride, K_b for water is $0.52 \text{ K kg mol}^{-1}$. (Atomic mass of K = 39, Cl = 35.5)
Answer. 374.077 K
- 12.5 g of the solute when dissolved in 170 g of water results in elevation of boiling point by 0.63 K. Calculate molecular mass of the solute. K_b for water = $0.52 \text{ K kg mol}^{-1}$.
Answer. 60.69
- The normal freezing point of nitrobenzene is 278.82 K. A 0.25 molal solution of a certain solute in nitrobenzene causes a freezing point depression of 2 degrees. Calculate the value of K_f for nitrobenzene.
Answer. 8 K kg mol^{-1}
- Calculate the amount of KCl which must be added to 1 kg of water so that the freezing point is depressed by 2K.
Answer. 80.1 g
- The boiling point of water is 100°C and it becomes 100.52°C if 3 g of a non-volatile solute is dissolved in 200 g of it. Calculate the molecular mass of the solute. (K_b for water = $0.52 \text{ K kg mol}^{-1}$).
Answer. 15
- The vapour pressure of methyl alcohol at 298 K is 96 torr. Its mole fraction in a solution with ethyl alcohol is 0.305, what is its vapour pressure if it obeys Raoult's law.
Answer. 29.28 torr
- Benzene and toluene form ideal solutions. At 323 K, the vapour pressure of pure benzene is 269 torr and that of pure toluene is 926 torr. What is the total vapour pressure at 323 K if a solution is prepared from 39.0 g benzene and 23 g toluene ?
Answer. 299.9 torr
- The capacity of the radiator of a car is 5 dm^3 . If the car is to be used in Srinagar when the temperature is 263.15 K, calculate the mass of ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) which must be added so that it does not freeze. K_f for water = 1.86 kg dm^3 .
Answer. 1.426 kg
- The vapour pressure of a dilute solution of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) is 750 mm of Hg at 373 K. Calculate the molality and mole fraction of the solute ?
Answer. 0.7404 m ; 0.132
- An aqueous solution contain 5 % and 10 % of urea and glucose respectively (by weight). Calculate the depression in freezing point of solution (K_f for water = 1.86°)
Answer. 3.03°C
- Benzene, C_6H_6 (boiling point 353.1 K) and toluene, C_7H_8 (boiling point 383.6) are two hydrocarbons that form a very nearly ideal solution. At 313 K, the vapour pressure of pure liquids are benzene = 160 mm Hg and toluene = 60 mm Hg. Assuming an ideal behaviour, calculate the partial pressures of benzene and toluene and the total pressure over the solution obtained by mixing equal number of moles of benzene and toluene.
Answer. 80 mm, 30 mm and 110 mm
- Ethyl alcohol and methyl alcohol form a solution which is almost ideal. The vapour pressure of ethyl alcohol is 44.5 mm and that of methyl alcohol is 88.7 mm at 293 K. Calculate the partial pressures and total pressure of the solution obtained by mixing 100 g of ethyl alcohol with 50 g of methyl alcohol.
Answer. 96.73 mm ; 138.59 mm ; 235.32 mm

14. An aqueous solution contains 30 % by weight of a liquid A (molecular mass 120) has a vapour pressure of 160 mm at 310 K. Find the vapour pressure of pure liquid A (the vapour pressure of water at 310 K is 150 mm)
Answer. 1715 mm
15. Calculate the Molal elevation constant for benzene if its boiling point is 353 K and ΔH_{vap} is 30.8 kJ mol⁻¹
Answer. 2.62 K kg mol⁻¹
16. The boiling point of a solution containing 2.56 g of substance A per 100 g of water is higher by 0.052 °C than the boiling point of pure water. Calculate the molar mass of the substance if molar elevation constant of water is 0.512 K kg mol⁻¹.
Answer. 252 g mol⁻¹
17. Calculate the molal depression constant of benzene if its enthalpy of fusion at 30.05 cal g⁻¹ and it freezes at 5.48 °C.
Answer. 5.11 K kg mol⁻¹
18. 50 g of sucrose is dissolved in 300 g of water. Calculate the boiling point and freezing point of the solution. ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta H_{vap} = 40.67 \text{ kJ mol}^{-1}$)
Answer. 100.26 °C ; - 0.95 °C
19. Calculate the amount of CS₂ present as an impurity in 50 g of Chloroform which raises the boiling point of Chloroform by 0.3 °C.
Answer. 3.14 g
20. Calculate the molar mass of a solute, 1 g of which in solution depresses the freezing point of benzene by 0.516 °C. ($K_f = 5.12 \text{ °C kg mol}^{-1}$)
Answer. 198.4
21. Phenol (C₆H₅OH) associates in water to form associated molecules. 0.6677g of phenol dissolved in 35.5 g of water decreases the freezing point of water by 0.215 °C. Calculate the degree of association of phenol. (K_f for water = 1.85°C kg mol⁻¹)
Answer. 83.8 %
22. The depression in freezing point of a solution containing 1.5 g of Barium nitrate [Ba(NO₃)₂] in 100 g of water is 0.72 °C. Calculate the degree of dissociation of the salt. K_f for water is 1.86 °C (At mass of Ba = 137, N = 14 and O = 16)
Answer. 0.81 or 81 %
23. A very small amount of non-volatile solute (that does not dissociate) is dissolved in 5.68 cm³ of benzene (density 0.889 g cm⁻³). At room temperature, vapour pressure of this solution is 98.85 mm Hg while that of benzene is 100 mm Hg. Find the molality of this solution. If the freezing point of this solution is 0.073° lower than that of benzene, what is the value of molal freezing point depression constant of benzene.
Answer. 0.144 m ; 5.7 K
24. Calculate the boiling point of a solution containing 0.61 g of benzene acid in 50 g of CS₂ assuming 84% dimerisation of the acid. The boiling point and K_b of CS₂ are 46.2 °C and 2.3 K kg mol⁻¹ respectively.
Answer. 46.333 °C
25. How much ethyl alcohol must be added to 1.00 litre of water so that the solution will freeze at 14° F ? (K_f for water = 1.86 °C /mole)
Answer. 247.3 g

16

Osmosis and Osmotic Pressure

CHAPTER

KEY CONCEPTS AND EQUATIONS



OSMOSIS

The flow of the solvent through a semipermeable membrane from pure solvent to solution or from a dilute solution to concentrated solution is termed Osmosis.

OSMOTIC PRESSURE

The hydrostatic pressure built up on the solution which just stops the osmosis of pure solvent into the solution through a semipermeable membrane is called Osmotic Pressure.

It may also be defined as the external pressure applied to the solution in order to stop the Osmosis of solvent into solution separated by a semipermeable membrane.

VAN'T HOFF EQUATION FOR SOLUTION

It has been shown by experiments that for n moles of the solute dissolved in V litres of the solution, the Osmotic pressure π at temperature T is given by

$$\pi V = n R T$$

where R is gas constant

$$\begin{aligned} \text{or} \quad \pi &= \frac{n R T}{V} \\ &= C R T \end{aligned}$$

where C is the molar concentration of the solution. At a given temperature, both R and T are constants. Therefore $\pi \propto C$

Thus osmotic pressure depends upon the molar concentration of solution and is, therefore, colligative property.

DETERMINATION OF MOLECULAR MASS FROM OSMOTIC PRESSURE MEASUREMENTS

According to van't Hoff equation.

$$\pi = \frac{n}{V} R T \quad \text{..... (i)}$$

where n is the number of moles of solute. It may be written as

$$n = \frac{w}{M}$$

where w is the mass of the solute and M its molecular mass. Substituting this in equation (i) we have

$$\pi = \frac{w}{M} \times \frac{RT}{V}$$

or molecular mass of the solute,
$$M = \frac{w R T}{V \times \pi}$$

ABNORMAL MOLECULAR MASSES

The molecular masses of some substances as determined experimentally by osmotic pressure measurements are different from those calculated theoretically from their chemical formula. In such cases either association or dissociation of molecules takes place. The number of particles decrease or increase as compared to the number of particles if no ionisation or association takes place. Since the osmotic pressure is a colligative property (dependent on the number of particles) it shows deviations. In such cases van't Hoff equation may be written as

$$\pi V = i n R T$$

where i is called van't Hoff factor and is given by

$$i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}$$

In case of association $i < 1$ and

in case of dissociation $i > 1$

The van't Hoff factor, i is related to the degree of dissociation, α , by the relation.

$$i = 1 + \alpha$$

The value of i will lie between 1 and 2.

RELATION BETWEEN OSMOTIC PRESSURE AND VAPOUR PRESSURE

It has been found experimentally that the osmotic pressure is directly proportional to the relative lowering of vapour pressure, *i.e.*

$$\pi \propto \frac{p - p_s}{p}$$

where p is the vapour pressure of the solvent and p_s , the vapour pressure of the solution at a given temperature.

RAOULT'S LAW AND THE OSMOTIC VAPOUR PRESSURE

We know

$$\pi V = n R T$$

or

$$\pi = \frac{n}{V} R T$$

and the relative lowering of vapour pressure is proportional to the osmotic pressure *i.e.*

$$\frac{p - p_s}{p} \propto \pi \quad \text{..... (ii)}$$

or

$$\frac{p - p_s}{p} = \frac{n}{N} \quad \text{..... (iii)}$$

where n is the number of moles of the solute and N the number of moles of solvent.

From equation (ii) and (iii) we have

$$\pi \propto \frac{n}{N}$$

This is Raoult's law equation.

ISOTONIC SOLUTIONS

Isotonic solutions are those solutions which have the same osmotic pressure. For two isotonic solution at the same temperature we have

$$C_1 = C_2$$

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. Calculate the osmotic pressure of a 5% solution of glucose at 27 °C.

SOLUTION :**Formula used**

$$\pi = \frac{n}{V} R T$$

Quantities given

$$n = \frac{5\text{g}}{180\text{g mol}^{-1}} = 0.02778 \text{ mol}$$

$$V = \frac{1}{10} \text{ lit} = 0.1 \text{ lit}$$

$$R = 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1}$$

$$T = 27 + 273 = 300\text{K}$$

Substitution of values

$$\begin{aligned} \pi &= \frac{0.02778 \text{ mol} \times 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{0.1 \text{ lit}} \\ &= \mathbf{6.8422 \text{ atm}} \end{aligned}$$

SOLVED PROBLEM 2. A 0.100 molal aqueous solution of NH_4Cl freezes at 0.344 °C. Calculate i . (

$$K_f = 1.86^\circ\text{C})$$

SOLUTION : (i) To calculate the molecular mass of the solute**Formula Used**

$$m = \frac{1000 \times K_f \times w}{W \times T_f}$$

Quantities given

$$K_f = 1.86^\circ\text{C}$$

$$w = 0.1\text{m} = 0.1\text{m} \times 53.5 \text{ g mol}^{-1} = 5.35 \text{ g}$$

$$\Delta T_f = 0.344^\circ\text{C}$$

$$W = 1000 \text{ g}$$

Substitution of values

$$\begin{aligned} m &= \frac{1000 \times 1.86^\circ\text{C} \times 5.35\text{g}}{1000\text{g} \times 0.344^\circ\text{C}} \\ &= \mathbf{28.9} \end{aligned}$$

ii) To calculate the van't Hoff factor i **Formula used**

$$i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}$$

$$= \frac{53.5}{28.9}$$

$$= 1.849$$

SOLVED PROBLEM 3. Calculate the osmotic pressure of a 5% solution of glucose ($C_6H_{12}O_6$) at $18^\circ C$. $R = 0.0820 \text{ atm lit K}^{-1} \text{ mol}^{-1}$.

SOLUTION :

Formula used

$$\pi = \frac{n}{V} R T$$

Quantities given

$$n = \frac{5\text{g}}{180 \text{ g mol}^{-1}} = 0.02778 \text{ mol}$$

$$V = \frac{1}{10} \text{ lit} = 0.10 \text{ lit}$$

$$T = 18 + 273 = 291 \text{ K}$$

$$R = 0.0820 \text{ atm lit K}^{-1} \text{ mol}^{-1}$$

Substitution of values

$$\pi = \frac{0.02778 \text{ mol} \times 0.0820 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 291 \text{ K}}{0.10 \text{ lit}}$$

$$= 6.628 \text{ atm}$$

SOLVED PROBLEM 4. An aqueous solution contains 20 g of glucose per litre. Calculate the pressure of the solution at $25^\circ C$ (molecular mass of glucose = 180).

SOLUTION :

Formula used

$$\pi = \frac{n}{V} R T$$

Quantities given

$$n = \frac{20\text{g}}{180 \text{ g mol}^{-1}} = 0.111 \text{ mol}$$

$$V = 1 \text{ lit.}$$

$$T = 25 + 273 = 298 \text{ K}$$

$$R = 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1}$$

Substitution of values

$$\pi = \frac{0.111 \text{ mol} \times 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{1 \text{ lit.}}$$

$$= 2.71 \text{ atm}$$

SOLVED PROBLEM 5. A 1% solution of potassium chloride is 80% dissociated. What is its osmotic pressure at 300 K ? ($R = 0.082 \text{ atm lit K}^{-1} \text{ mol}^{-1}$; $K = 39$; $Cl = 35.5$)

SOLUTION : (i) To calculate the van't Hoff factor, i

$$\text{No. of moles of KCl in 1\% solution} = \frac{1 \text{ g}}{74.5 \text{ g mol}^{-1}} = 0.01342 \text{ mol}^{-1}$$

	KCl	→	K	+	Cl ⁻
Initial Concentration	0.01342		0		0
Final Concentration	(0.01342 - α)		0.01342α		0.01342α

$$\begin{aligned}\text{Total number of particles} &= 0.01342(1-\alpha) + 0.01342\alpha + 0.01342\alpha \\ &= 0.01342(1+\alpha)\end{aligned}$$

Since $\alpha = 80\%$ or 0.8, we have

$$\begin{aligned}\text{Total number of particles} &= 0.01342(1+0.8) \\ &= 0.024126\end{aligned}$$

$$\begin{aligned}\text{van't Hoff factor, } i &= \frac{0.024126}{0.01342} \\ &= 1.80\end{aligned}$$

(ii) To calculate the osmotic pressure

Formula used

$$\pi = \frac{i n R T}{V}$$

Quantities given

$$\begin{aligned}i &= 1.8 & n &= 0.01342 \text{ mol} & V &= \frac{1}{10} \text{ lit} = 0.1 \text{ lit} \\ R &= 0.082 \text{ atm lit K}^{-1} \text{ mol}^{-1} & T &= 300 \text{ K}\end{aligned}$$

Substitution of values

$$\begin{aligned}\pi &= \frac{1.8 \times 0.01342 \text{ mol} \times 0.082 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{0.1 \text{ lit}} \\ &= \mathbf{5.94 \text{ atm}}\end{aligned}$$

SOLVED PROBLEM 6. Calculate the molality and osmotic pressure of 0.5% solution of urea (molecular mass = 60) in water at 0 °C. ($R = 0.082 \text{ atm lit K}^{-1} \text{ mol}^{-1}$).

SOLUTION : (i) To calculate the molality

Formula used

$$\text{molality, } m = \frac{\text{mass of urea} \times 1000}{\text{mol mass of urea} \times \text{mass of solvent}}$$

Quantities given

$$\begin{aligned}\text{mass of urea} &= 0.5 \text{ g} & \text{mass of solvent} &= 99.5 \text{ g} \\ \text{mol mass of urea} &= 60 \text{ g mol}^{-1}\end{aligned}$$

Substitution of values

$$\begin{aligned}\text{molality, } m &= \frac{0.5 \text{ g} \times 1000}{60 \text{ g mol}^{-1} \times 99.5 \text{ g}} \\ &= 0.0838 \text{ m}\end{aligned}$$

(ii) To calculate the osmotic pressure

Formula used

$$\pi = \frac{n}{V} R T$$

Quantities given

$$n = \frac{0.5 \text{ g}}{60 \text{ g mol}^{-1}} = 0.00833 \text{ mol}$$

$$R = 0.082 \text{ atm lit K}^{-1} \text{ mol}^{-1}$$

$$V = \frac{1}{10} \text{ lit} = 0.1 \text{ lit}$$

$$T = 273 \text{ K}$$

Substitution of values

$$\begin{aligned} \pi &= \frac{0.00833 \text{ mol} \times 0.082 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 273 \text{ K}}{0.1 \text{ lit}} \\ &= 1.86 \text{ atm} \end{aligned}$$

SOLVED PROBLEM 7. Calculate the osmotic pressure of 0.01 M solution of cane sugar at 30 °C.

SOLUTION :

Formula used

$$\pi = C R T$$

Quantities given

$$C = 0.01 \text{ M}$$

$$R = 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \quad T = 30 + 273 = 303 \text{ K}$$

Substitution of values

$$\begin{aligned} \pi &= 0.01 \text{ mol} \times 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 303 \text{ K} \\ &= \mathbf{0.249 \text{ atm}} \end{aligned}$$

SOLVED PROBLEM 8. What is the concentration of cane sugar which is isotonic with solution containing 6 g of urea per litre? (mol mass of urea and cane sugar are 60 and 340 respectively).

SOLUTION : (i) To calculate the osmotic pressure of urea solution

Formula used

$$\pi = \frac{n}{V} R T$$

Quantities given

$$n = \frac{6 \text{ g}}{60 \text{ g mol}^{-1}} = 0.1 \text{ mol}$$

$$V = 1 \text{ lit}$$

Substitution of values

$$\begin{aligned} \pi &= \frac{0.1 \text{ mol} \times R \times T}{1 \text{ lit}} \\ &= 0.1 R T \end{aligned}$$

(ii) To calculate the concentration of cane sugar

Formula used

$$\pi = C R T$$

Quantities given

$$\pi = 0.1 R T$$

Substitution of values

$$0.1 R T = C R T$$

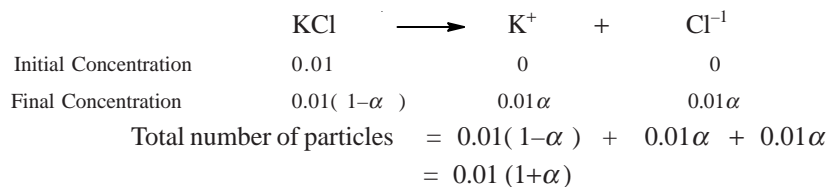
or

$$\begin{aligned} C &= 0.1 \text{ mol} \\ &= \frac{342}{10} \text{ g lit}^{-1} \\ &= \mathbf{34.2 \text{ g lit}^{-1}} \end{aligned}$$

SOLVED PROBLEM 9. Calculate the osmotic pressure of 0.745% solution of KCl at 27 °C assuming to be 86% dissociated.

SOLUTION : (i) To calculate the van't Hoff factor i

$$\text{Number of moles of KCl in 0.745\% solution} = \frac{0.745 \text{ g}}{74.5 \text{ g mol}^{-1}} = 0.01 \text{ mol}$$



Since $\alpha = 86\%$ or 0.86, we have

$$\begin{aligned} \text{Total number of particles} &= 0.01(1 + 0.86) \\ &= 0.0186 \end{aligned}$$

$$\text{van't Hoff factor, } i = \frac{0.0186}{0.01} = 1.86$$

(ii) To calculate the osmotic pressure

Formula used

$$\pi = i \frac{n}{V} R T$$

Quantities given

$$i = 1.86$$

$$n = 0.01 \text{ m}$$

$$T = 300 \text{ K}$$

$$R = 0.0820 \text{ atm lit K}^{-1} \text{ mol}^{-1}$$

$$V = \frac{1}{10} \text{ lit} = 0.01 \text{ lit}$$

Substitution of values

$$\begin{aligned} \pi &= \frac{1.86 \times 0.01 \text{ m} \times 0.0820 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{0.10 \text{ lit}} \\ &= 4.576 \text{ atm} \end{aligned}$$

SOLVED PROBLEM 10. Is 5% solution of cane sugar (mol mass = 342) isotonic with 0.877% solution of urea?

Formula used

$$\pi = \frac{n}{V} R T$$

Quantities given

$$n = \frac{5 \text{ g}}{342 \text{ g mol}^{-1}} = 0.01462 \text{ mol}$$

$$V = \frac{1}{10} \text{ lit} = 0.1 \text{ lit}$$

Substitution of values

$$\begin{aligned} \pi &= \frac{0.01462 \text{ mol}^{-1}}{0.1 \text{ lit}} R T \\ &= 0.1462 R T \end{aligned}$$

(ii) To calculate the osmotic pressure of 8.77% urea solution

Quantities given

$$n = \frac{0.877 \text{ g}}{60 \text{ g mol}^{-1}} = 0.1462 \text{ mol}$$

$$V = \frac{1}{10} \text{ lit} = 0.1 \text{ lit}$$

Substitution of values

$$\begin{aligned}\pi &= \frac{0.1462 \text{ mol} \times R T}{0.1 \text{ lit}} \\ &= \mathbf{1.462 R T}\end{aligned}$$

Since both solutions have the same osmotic pressure, they are isotonic.

SOLVED PROBLEM 11. Calculate the concentration (g/litre) of aqueous glucose (mol mass = 180) which is isotonic with blood (Osmotic pressure for blood is 7.65 atm at 37 °C and $R = 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1}$)

SOLUTION :

Formula used

$$\pi = C R T \quad \text{or} \quad C = \frac{\pi}{R T}$$

Quantities given

$$\pi = 7.65 \text{ atm}$$

$$R = 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1}$$

$$T = 310 \text{ K}$$

Substitution of values

$$\begin{aligned}C &= \frac{7.65 \text{ atm}}{0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 310 \text{ K}} \\ &= 0.3005 \text{ mol lit}^{-1} \\ &= 0.3005 \times 180 \text{ g lit}^{-1} \quad [\because 1 \text{ mol of glucose} = 180 \text{ g}] \\ &= \mathbf{54.1 \text{ g lit}^{-1}}\end{aligned}$$

SOLVED PROBLEM 12. Calculate osmotic pressure of solution at 25 °C containing (i) 5.85g of NaCl and (ii) 5.0 g of urea per litre of solution.

SOLUTION : (i) To calculate the osmotic pressure of NaCl solution

Formula used

$$\pi = \frac{n}{V} R T$$

Quantities given

$$n = \frac{5.85 \text{ g}}{58.5 \text{ g mol}^{-1}} = 0.1 \text{ m}$$

$$R = 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1}$$

$$T = 25 + 273 = 298 \text{ K}$$

$$V = 1 \text{ lit}$$

Substitution of values

$$\begin{aligned}\pi &= \frac{0.1 \text{ mol} \times 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{1 \text{ lit}} \\ &= \mathbf{2.45 \text{ atm}}\end{aligned}$$

(ii) To calculate the osmotic pressure of urea solution

Quantities given

$$n = \frac{5 \text{ g}}{60 \text{ g mol}^{-1}} = 0.0833 \text{ mol}$$

$$R = 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1}$$

$$T = 25 + 273 = 298 \text{ K}$$

$$V = 1 \text{ litre}$$

Substitution of values

$$\begin{aligned}\pi &= \frac{0.0833 \text{ mol} \times 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{1 \text{ lit}} \\ &= \mathbf{2.038 \text{ atm}}\end{aligned}$$

SOLVED PROBLEM 13. 10 g of urea of molecular mass 60 is dissolved in one litre of water.

Calculate the osmotic pressure of the solution at 20 °C.

SOLUTION :

Formula used

$$\pi = \frac{n}{V} R T$$

Quantities given

$$n = \frac{10 \text{ g}}{60 \text{ g mol}^{-1}} = 0.1667 \text{ mol}$$

$$R = 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1}$$

$$T = 20 + 273 = 293 \text{ K}$$

$$V = 1 \text{ lit}$$

Substitution of values

$$\begin{aligned} \pi &= \frac{0.1667 \text{ mol} \times 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 293 \text{ K}}{1 \text{ lit}} \\ &= \mathbf{4.01 \text{ atm}} \end{aligned}$$

SOLVED PROBLEM 14. A solution containing 8.6 g per dm³ of urea (mol mass 60) was found to be isotonic with a 5% solution of an organic non-volatile solution. Calculate the molecular mass of the latter.

SOLUTION :

Formula used

$$\pi = \frac{n}{V} R T$$

(i) For urea

Quantities given

$$n = \frac{8.6 \text{ g}}{60 \text{ g mol}^{-1}} = 0.1433 \text{ mol}$$

$$V = 1 \text{ lit}$$

Substitution of values

$$\pi = \frac{0.1433 \text{ mol } R T}{1 \text{ lit}} = 0.1433 R T$$

(ii) For organic non-volatile solute

Quantities given

$$n = \frac{5 \text{ g}}{M \text{ g mol}^{-1}} = \frac{5}{M} \text{ mol}$$

$$V = 0.1 \text{ lit}$$

Substitution of values

$$\pi = \frac{5/M \text{ mol}^{-1} \times R T}{0.1 \text{ lit}} = \frac{50}{M} R T$$

Since both solutions are isotonic we have

$$0.1433 R T = \frac{50}{M} R T$$

or

$$\begin{aligned} M &= \frac{50}{0.1433} \\ &= \mathbf{348.9} \end{aligned}$$

SOLVED PROBLEM 15. A solution contains 5g of urea (mol mass 60) per 100g of water. If the density of water at 25 °C is 0.998 g cm⁻³, calculate the osmotic pressure of the solution at the same temperature ($R = 0.082 \text{ atm lit K}^{-1} \text{ mol}^{-1}$).

SOLUTION : (i) To calculate the volume of 100g of water

$$\begin{aligned}
 \text{Density of water} &= 0.998 \text{ g cm}^{-3} \\
 \text{Volume of 100g of water} &= 100 \text{ g} \div 0.998 \text{ g cm}^{-3} & [\because V = \frac{M}{D}] \\
 &= 100.2 \text{ cm}^3 \\
 &= 0.1002 \text{ lit} & [\because 1 \text{ lit} = 1000 \text{ cm}^3]
 \end{aligned}$$

(ii) To calculate the osmotic pressure**Formula used**

$$\pi = \frac{n}{V} R T$$

Quantities given

$$\begin{aligned}
 n &= \frac{5 \text{ g}}{60 \text{ g mol}^{-1}} = 0.0833 \text{ mol} & R &= 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \\
 T &= 25 + 273 = 298 \text{ K} & V &= 0.1002 \text{ lit}
 \end{aligned}$$

Substitution of values

$$\begin{aligned}
 \pi &= \frac{0.0833 \text{ mol} \times 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}{0.1002 \text{ lit}} \\
 &= \mathbf{20.34 \text{ atm}}
 \end{aligned}$$

SOLVED PROBLEM 16. 3.58 g of NaCl was dissolved in 120 g of water at 77 °C. If the osmotic pressure of solution is 26.31 atm, then calculate the degree of dissociation of NaCl.

SOLUTION : (i) To calculate van't Hoff Factor, i **Formula used**

$$\pi = i \frac{n}{V} R T$$

Quantities given

$$\begin{aligned}
 \pi &= 26.31 \text{ atm} & R &= 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} & T &= 77 + 273 = 350 \text{ K} \\
 n &= \frac{3.58 \text{ g}}{58.5 \text{ g mol}^{-1}} = 0.0612 \text{ mol} & V &= \frac{120}{1000} = 0.12 \text{ lit}
 \end{aligned}$$

Substitution of values

$$26.31 \text{ atm} = i \times \frac{0.0612 \text{ mol} \times 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 350 \text{ K}}{0.12 \text{ lit}}$$

$$\text{or} \quad i = 1.7954$$

(ii) To calculate the degree of dissociation**Formula used**

$$\begin{aligned}
 i &= 1 + \alpha \\
 \text{or} \quad \alpha &= i - 1 \\
 &= 1.7954 - 1 \\
 &= \mathbf{0.7954 \text{ or } 79.54 \%}
 \end{aligned}$$

SOLVED PROBLEM 17. A 5% solution of cane sugar (mol mass 342) is isotonic with 0.877% solution of substance X. Find out the molecular mass of X.

SOLUTION :

$$\begin{aligned}\text{Concentration of cane sugar} &= \frac{50 \text{ g lit}^{-1}}{342 \text{ g mol}^{-1}} \\ &= \frac{50}{342} \text{ mol lit}^{-1}\end{aligned}$$

$$\begin{aligned}\text{Concentration of unknown substance} &= 0.877 \text{ g/100 ml} \\ &= 8.77 \text{ g lit}^{-1} \\ &= \frac{8.77 \text{ g lit}^{-1}}{M \text{ g mol}^{-1}} \\ &= \frac{8.77}{M} \text{ mol lit}^{-1}\end{aligned}$$

Since both solutions are isotonic, their concentration must be equal *i.e.*

$$\frac{50}{342} \text{ mol lit}^{-1} = \frac{8.77}{M} \text{ mol lit}^{-1}$$

$$\begin{aligned}\text{or} \quad M &= \frac{342 \times 8.77}{50} \\ &= \mathbf{60}\end{aligned}$$

SOLVED PROBLEM 18. Calculate the osmotic pressure of glucose containing 1.75 in 150 ml of solution at 17 °C.

SOLUTION :**Formula used**

$$\pi = \frac{n}{V} R T$$

Quantities given

$$n = \frac{1.75 \text{ g}}{180 \text{ g mol}^{-1}} = 0.009722 \text{ mol}$$

$$V = 150 \text{ ml} = 0.15 \text{ lit}$$

$$R = 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1}$$

$$T = 17 + 273 = 290 \text{ K}$$

Substitution of values

$$\begin{aligned}\pi &= \frac{0.009722 \text{ mol} \times 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 290 \text{ K}}{0.15 \text{ lit}} \\ &= \mathbf{1.543 \text{ atm}}\end{aligned}$$

SOLVED PROBLEM 19. Calculate the freezing point of an aqueous solution of a non-electrolyte having an osmotic pressure of 2.0 atm at 300 K. ($K_f = 1.86 \text{ K kg mol}^{-1}$; $R = 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1}$).

SOLUTION : (i) To calculate the concentration of the solution**Formula used**

$$\pi = C R T \quad \text{or} \quad C = \frac{\pi}{R T}$$

Quantities given

$$\pi = 2.0 \text{ atm}$$

$$R = 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1}$$

$$T = 300 \text{ K}$$

Substitution of values

$$C = \frac{2.0 \text{ atm}}{0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}$$

$$\begin{aligned} &= 0.0812 \text{ mol lit}^{-1} \\ \text{molality, } m &= 0.0812 \text{ mol kg}^{-1} \quad [\because 1 \text{ lit H}_2\text{O} = 1 \text{ kg H}_2\text{O}] \end{aligned}$$

(ii) To calculate the depression in freezing point**Formula used**

$$\Delta T_f = K_f \times m$$

Quantities given

$$m = 0.0812 \text{ mol kg}^{-1} \quad K_f = 1.86 \text{ K kg mol}^{-1}$$

Substitution of values

$$\begin{aligned} \Delta T_f &= 1.86 \text{ K kg mol}^{-1} \times 0.0812 \text{ mol kg}^{-1} \\ &= 0.151 \text{ K} \end{aligned}$$

$$\begin{aligned} \therefore \text{Freezing Point of solution} &= 273 \text{ K} - 0.151 \text{ K} \\ &= \mathbf{272.849 \text{ K}} \end{aligned}$$

ADDITIONAL PRACTICE PROBLEMS

- Calculate the osmotic pressure of 2% solution of glucose in water at 25 °C. Molecular mass of glucose = 180; $R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$)
Answer: $2.75 \times 10^5 \text{ Nm}^{-2}$
- A solution of sucrose (mol mass 342 g mol^{-1}) is prepared by dissolving 30 g of it per litre of solution. Calculate the osmotic pressure at 300 K ($R = 0.082 \text{ atm lit K}^{-1} \text{ mol}^{-1}$).
Answer: 2.15 atm
- A solution containing 3.0 g of a solute in 100 cm^3 of the solution exhibits an osmotic pressure of 2.05 atm at 27 °C. Calculate the molecular mass of the solute.
Answer: 360
- The osmotic pressure of a solution containing 2.0 g of protein in 200 ml of aqueous solution is 0.2 atm at 300K. Calculate the molar mass of the protein. ($R = 0.082 \text{ atm lit K}^{-1} \text{ mol}^{-1}$)
Answer: 1230 g mol^{-1}
- Calculate the molecular mass of a solute when 10 g of it is present in 100 ml of the solution at 27 °C which has an osmotic pressure of 2.85 atm. $R = 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1}$.
Answer: 864
- Osmotic pressure of a solution containing 2.0 g of dissolved protein in 250 ml of solution is 20 mm of Hg at 300 K. Calculate the molecular mass of the protein. ($R = 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1}$)
Answer: 7487
- Calculate the osmotic pressure of a mixture solution obtained by mixing 1 litre of 7.5% solution of substance A with mol mass = 75 and two litres of a 5% solution of substance B (with molecular mass 60 at 453 K.)
Answer: 7.95 atm

8. Calculate the osmotic pressure of a glucose solution containing 15 g in 100 ml solution at 27 °C.
Answer. 20.5 atm
9. An aqueous solution contains 20 g of glucose in one litre of the solution. Assuming the solution to be ideal, calculate its osmotic pressure at 25 °C.
Answer. 2.718 atm
10. Calculate the osmotic pressure of a sugar solution in which 3.42 g of sugar has been dissolved in 100 cm³ of solution at 300 K.
Answer. 2.477 atm
11. The osmotic pressure of solution containing 5×10^{-3} kg sugar in 250 cm³ is 1.45×10^5 Nm⁻² at 298 K. What is the molar mass of sugar cane ?
Answer. 341.7 g mol⁻¹
12. A 1.8% solution of an unknown solute is isotonic with 10.26% solution of sugar cane (molecular mass = 342). Calculate the molar mass of the solute.
Answer. 60 g mol⁻¹
13. The average osmotic pressure of human blood at body temperature 37 °C is 7.6 atm. Calculate the total concentration of various solutes in blood.
Answer. 0.298 mol⁻¹
14. Calculate the osmotic pressure of a 10% solution of urea (molecular mass = 60; $R = 0.0821$ atm lit K⁻¹mol⁻¹) at 300 K.
Answer. 40.05 atm
15. Calculate the osmotic pressure of a solution obtained by mixing 100 ml of 5% solution of urea (molecular mass = 60) and 100 ml of 4% solution of sucrose at 300 K. (molecular mass = 342) $R = 0.0821$ atm lit K⁻¹ mol⁻¹)
Answer. 11.70 atm
16. Calculate the osmotic pressure of a solution at 25 °C obtained by mixing 100 cm³ of 4.6 % of glucose and 200 cm³ of 4.5% solution of glucose.
Answer. 8.332 atm
17. The formula for starch is $(C_6H_{10}H_5)_n$ where $n = 200$. When 1.0 g of starch is dissolved in 100 ml of water solution, what is the osmotic pressure of 27 °C ?
Answer. 7.60×10^{-3} atm
18. The osmotic pressure of blood at 37 °C is 7.6 atm. A solution that is given intravenously must have the same osmotic pressure as blood. What should be the molarity of a glucose solution to give an osmotic pressure of 7.6 atm at 37 °C ?
Answer. 0.298 mol⁻¹

19. A solution containing 4 g of a non-volatile organic solute per litre was found to have an osmotic pressure 360mm of Hg at 27 °C. Calculate the molecular mass of the solute.

Answer. 197

20. A 5% solution of glucose (molecular mass 60) is isotonic with 3% solution of an unknown compound. Calculate the molecular mass of the unknown substance.

Answer. 36

21. A solution of sucrose (molar mass 342 g mol^{-1}) is prepared by dissolving 68.4 of it per litre of the solution. What is its osmotic pressure at 300 K ? ($R = 0.082 \text{ lit atm deg}^{-1} \text{ mol}^{-1}$)

Answer. 4.92 atm

22. A 1.2% solution of NaCl is isotonic with 7.2% solution of glucose. Calculate van't Hoff factor of NaCl solution .

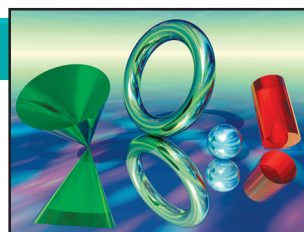
Answer. 1.95

17

Chemical Equilibrium

CHAPTER

KEY CONCEPTS AND EQUATIONS



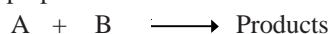
CHEMICAL EQUILIBRIUM

The state of a reversible reaction when the two opposing reactions occur at the same rate is called Chemical equilibrium. At equilibrium the concentrations of reactants and products do not change with time. Thus at equilibrium

$$\text{Rate of forward reaction} = \text{Rate of backward reaction}$$

LAW OF MASS ACTION

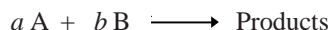
The rate of a chemical reaction is proportional to the active masses of the reactants. For the reaction



we can write

$$\text{Rate of reaction} \propto [A] [B] = k [A] [B]$$

and for the reaction



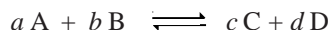
we have

$$\text{Rate of reaction} \propto [A]^a [B]^b = K [A]^a [B]^b$$

EQUILIBRIUM CONSTANT

The product of the equilibrium concentration of the products divided by the product of the equilibrium concentrations of the reactants, with each concentration term raised to a power equal to the coefficient of the substance in the balance equation is called the Equilibrium constant.

For the reaction

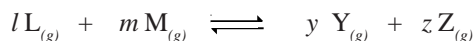


the equilibrium constant is given by

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

EQUILIBRIUM CONSTANT IN TERMS OF PARTIAL PRESSURE

The partial pressure of a gas in the equilibrium mixture is directly proportional to its molar concentration at a given temperature. For the reaction

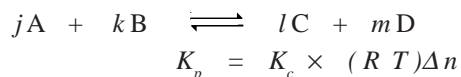


the equilibrium constant K_p is given by

$$K_p = \frac{(p_Y)^y (p_Z)^z}{(p_L)^l (p_M)^m}$$

RELATION BETWEEN K_p AND K_c

For the reaction



where

$$\Delta n = (l + m) - (j + k)$$

when

$$\Delta n = 0 \quad K_p = K_c$$

RELATION BETWEEN ΔG AND THE EQUILIBRIUM CONSTANT

The change in free energy of a reaction and the equilibrium constant K are related to each other by the relation

$$\Delta G = -RT \ln K$$

Case I when ΔG is -ve the forward reaction is spontaneous.

Case II when ΔG is 0 the reaction is at equilibrium.

Case III when ΔG is +ve the reverse reaction is spontaneous.

TEMPERATURE DEPENDENCE OF EQUILIBRIUM CONSTANT (VAN'T HOFF EQUATION)

The value of equilibrium constant changes with temperature. The relation between equilibrium constants at two different temperatures and the enthalpy change is given by

$$\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

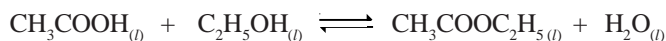
where K_{p_2} is the equilibrium constant at temperature T_2 and K_{p_1} is the equilibrium constant at temperature T_1

In terms of ΔE the equation becomes

$$\log \frac{K_{c_2}}{K_{c_1}} = \frac{\Delta E}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

LIQUID SYSTEMS

The reaction between acetic acid and ethyl alcohol to form ethyl acetate and water is represented by



Initial conc. a b 0 0

Eq. conc. $a - x$ $b - x$ x x

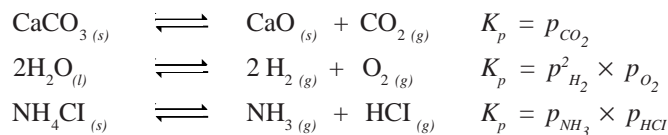
The equilibrium constant may be written as

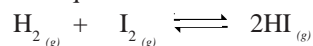
$$K = \frac{\frac{x}{V} \times \frac{x}{V}}{\left(\frac{a-x}{V}\right) \times \left(\frac{b-x}{V}\right)} \quad \text{or} \quad \frac{x^2}{(a-x)(b-x)}$$

where V is the volume

HETEROGENEOUS EQUILIBRIA

The equilibria in which the reactants and products are not all in the same phase are called heterogeneous equilibria. The examples with their equilibrium constants are



ADDITIONAL SOLVED PROBLEMS**SOLVED PROBLEM 1.** The equilibrium constant at 444 °C for the reactionis 1.39×10^{-2} . Calculate the equilibrium constant at the same temperature for the reaction**SOLUTION :****Formula used**

$$K' = \frac{1}{K}$$

Quantity given

$$K = 1.39 \times 10^{-2}$$

Substitution of value

$$\begin{aligned} K' &= \frac{1}{1.39 \times 10^{-2}} \\ &= \frac{100}{1.39} \\ &= \mathbf{71.94} \end{aligned}$$

SOLVED PROBLEM 2. One mole of PCl_5 is heated in closed two-litre vessel. At equilibrium40% of PCl_5 is dissociated. Calculate the equilibrium constant of the reaction**SOLUTION :**The dissociation of PCl_5 is represented by

Initial concentration	1.0 mole	0	0
Equilibrium concentration	0.6 mole	0.4 mole	0.4 mole

Formula used

$$K = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$

Quantities given

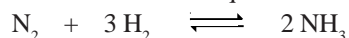
$$[\text{PCl}_5] = \frac{0.6 \text{ mole}}{2 \text{ lit}} = 0.3 \text{ mol lit}^{-1}$$

$$[\text{PCl}_3] = \frac{0.4 \text{ mole}}{2 \text{ lit}} = 0.2 \text{ mol lit}^{-1}$$

$$[\text{Cl}_2] = \frac{0.4 \text{ mole}}{2 \text{ lit}} = 0.2 \text{ mol lit}^{-1}$$

Substitution of value

$$\begin{aligned} K &= \frac{0.2 \text{ mol lit}^{-1} \times 0.2 \text{ mol lit}^{-1}}{0.3 \text{ mol lit}^{-1}} \\ &= \mathbf{0.133 \text{ mol lit}^{-1}} \end{aligned}$$

SOLVED PROBLEM 3. The concentration equilibrium constant K_c for the reactionat 400 °C is 0.5. Find the value of K_p ($R = 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1}$)**SOLUTION :****Formula used**

$$K_p = K_c \times (RT)^{\Delta n}$$

Quantities given

$$\Delta n = n_p - n_R = 2 - 4 = -2$$

$$K_c = 0.5$$

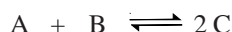
$$T = 400 + 273 = 673 \text{ K}$$

$$R = 0.0821 \text{ atm lit K}^{-1} \text{ mol}^{-1}$$

Substitution of values

$$\begin{aligned} K_p &= 0.5 \times (0.0821 \times 673)^{-2} \\ &= 0.5 \times (55.2533)^{-2} \\ &= \mathbf{0.000164} \end{aligned}$$

SOLVED PROBLEM 4. Calculate the equilibrium constant of the reaction from the data given below:



The reaction was started with 2.0 moles litre⁻¹ of A and 2.0 moles litre⁻¹ of B and the equilibrium constant of C was found to be 0.32 mol litre⁻¹.

SOLUTION : The equilibrium reaction is

	A	+	B	\rightleftharpoons	2 C
Initial conc.	2.0 mole		2.0 mole		0
Eq. conc.	1.84 mole		1.84 mole		0.32 mole

Formula used

$$K = \frac{[\text{C}]^2}{[\text{A}] [\text{B}]}$$

Quantities given

$$[\text{C}] = 0.32 \text{ mol lit}^{-1}$$

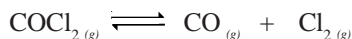
$$[\text{A}] = 1.84 \text{ mol lit}$$

$$[\text{B}] = 1.84 \text{ mol lit}^{-1}$$

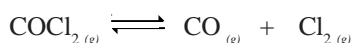
Substitution of values

$$\begin{aligned} K &= \frac{(0.32 \text{ mol lit}^{-1})^2}{(1.84 \text{ mol lit}^{-1}) \times (1.84 \text{ mol lit}^{-1})} \\ &= \mathbf{0.0302 \text{ mol lit}^{-1}} \end{aligned}$$

SOLVED PROBLEM 5. Calculate the ratio of K_p to K_c at 27 °C for the equilibrium reaction :

**SOLUTION :**

The equilibrium reaction is

**Formula used**

$$K_p = K_c (RT)^{\Delta n} \quad \text{or} \quad \frac{K_p}{K_c} = (RT)^{\Delta n}$$

Quantities given

$$\Delta n = n_p - n_R = 2 - 1 = 1 \text{ mole}$$

$$R = 0.082 \text{ atm lit K}^{-1} \text{ mol}^{-1}$$

$$T = 27 + 273 = 300 \text{ K}$$

Substitution of values

$$\begin{aligned} \frac{K_p}{K_c} &= (0.082 \times 300)^{-1} \\ &= (24.63)^{-1} = \mathbf{0.406} \end{aligned}$$

SOLVED PROBLEM 6. On heating in a closed vessel PCl_5 dissociates into PCl_3 & Cl_2 . At 200 °C the vapour density of the gaseous mixture is 75.5 Calculate the degree of dissociation of PCl_5 (P=31; Cl=35.5).

SOLUTION :**Formula used**

$$\frac{\rho_1}{\rho_2} = \frac{1+x}{1}$$

Quantities given

$$\rho_1, \text{ the density of undissociated gas} = \frac{\text{mol. mass of } \text{PCl}_5}{2} = \frac{31+5 \times 35.5}{2} = 104.25$$

$$\rho_2, \text{ the density of dissociated gas} = 75.5$$

Substitution of values

$$\frac{104.25}{74.5} = \frac{1+x}{1}$$

$$\text{or} \quad 1.399 = 1+x$$

$$\begin{aligned} \text{or} \quad x &= 1.399 - 1 \\ &= \mathbf{0.399} \end{aligned}$$

SOLVED PROBLEM 7. Calculate the free energy change (ΔG°) associated with chemical reaction for which the equilibrium constant at 298 K is 0.01 ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

SOLUTION :**Formula used**

$$\Delta G^\circ = -2.303 R T \log K$$

Quantities given

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

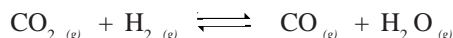
$$T = 298 \text{ K}$$

$$K = 0.01$$

Substitution of values

$$\begin{aligned} \Delta G^\circ &= -2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}^{-1} \times \log 0.01 \\ &= -5705.84 \text{ J} \times \log 0.01 \\ &= -5705.84 \text{ J} \times -2 \\ &= \mathbf{11411.68 \text{ J}} \end{aligned}$$

SOLVED PROBLEM 8. For the reaction



The equilibrium constant at 1000 K is 0.53.

(a) If a mixture at equilibrium in a 1 dm^3 vessel contains 0.25 mole of CO, 0.5 mole of CO_2 and 0.6 mole of H_2 , how many moles of H_2O are there in the vessel ?

(b) 5 moles of inert gas are added to the equilibrium mixture containing 1 mole of H_2 and 1 mole of CO_2 . Predict the equilibrium concentration of CO_2 and H_2O .

SOLUTION : (a)**Formula used**

$$K = \frac{[\text{CO}] [\text{H}_2\text{O}]}{[\text{CO}_2] [\text{H}_2]}$$

Quantities given

$$K = 0.53$$

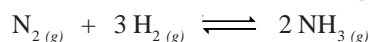
$$[\text{CO}] = 0.25$$

$$[\text{CO}_2] = 0.5$$

$$[\text{H}_2] = 0.6$$

Substitution of values

$$\begin{aligned}
 0.53 &= \frac{0.25 \times [H_2O]}{0.5 \times 0.6} \\
 [H_2O] &= \frac{0.53 \times 0.5 \times 0.6}{0.25} \\
 &= \mathbf{0.636}
 \end{aligned}$$

SOLVED PROBLEM 9. The equilibrium constant K_p for the reaction

is 1.64×10^{-4} at 673 K and 0.144×10^{-4} at 773 K. Calculate the mean heat of formation of ammonia from its elements in this temperature range.

SOLUTION :**Formula used**

$$\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H}{2.303 R} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$$

Quantities given

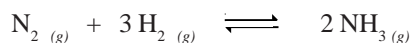
$$\begin{array}{lll}
 K_{p_2} = 0.144 \times 10^{-4} & T_2 = 773 \text{ K} & R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \\
 K_{p_1} = 1.64 \times 10^{-4} & T_1 = 673 \text{ K} &
 \end{array}$$

Substitution of values

$$\begin{aligned}
 \log \frac{0.144 \times 10^{-4}}{1.64 \times 10^{-4}} &= \frac{\Delta H}{2.303 \times 8.314} \left[\frac{773 - 673}{773 \times 673} \right] \\
 1.05648 &= \frac{\Delta H}{19.14714} \left[\frac{100}{673 \times 773} \right] \\
 \text{or } \Delta H &= - \frac{1.05648 \times 19.14714 \times 673 \times 773}{100} \\
 &= \mathbf{-105.235 \text{ kJ}}
 \end{aligned}$$

This is the heat of reaction in which two moles of NH_3 are formed.

$$\begin{aligned}
 \text{The mean heat of formation of } NH_3 &= - \frac{105.235 \text{ kJ}}{2} \\
 &= \mathbf{-52.6174 \text{ kJ}}
 \end{aligned}$$

SOLVED PROBLEM 10. For the reaction

K_p is 1.64×10^{-4} at 673 K. Calculate (i) ΔG ; (ii) ΔG when the partial pressure of N_2 , H_2 and NH_3 are 10 atm, 30 atm and 3 atm respectively; (iii) Is the reaction spontaneous?

SOLUTION :**(i) To calculate ΔG** **Formula used**

$$\Delta G = -2.303 RT \log K_p$$

Quantities given

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \quad T = 673 \text{ K} \quad K_p = 1.64 \times 10^{-4}$$

Substitution of values

$$\begin{aligned}
 \Delta G &= -2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 673 \text{ K} \times \log (1.64 \times 10^{-4}) \\
 &= -12886.027 \text{ J} \times (-3.78515) \\
 &= 48775.5 \text{ J} \\
 &= \mathbf{48.7755 \text{ J}}
 \end{aligned}$$

(ii) To calculate ΔG when partial pressures are given**Formula used**

$$\Delta G = -2.303 RT \log K_p$$

Quantities given

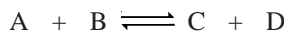
$$K_p = \frac{P_{NH_3}^2}{P_{N_2} \times P_{H_2}^3} = \frac{3^2}{10 \times 30^3} = 0.0000333 = 3.33 \times 10^{-5}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T = 673 \text{ K}$$

Substitution of values

$$\begin{aligned}
 \Delta G &= -2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 673 \text{ K} \times \log (3.33 \times 10^{-5}) \\
 &= -12886.027 \text{ J} \times (-4.47755) \\
 &= 57697.8 \text{ J} \\
 &= \mathbf{57.6978 \text{ kJ}}
 \end{aligned}$$

(iii) No - the reaction is not spontaneous since ΔG is positive.**SOLVED PROBLEM 11.** The equilibrium constant K_p for a reaction

is 10^{-12} at 327°C and 10^{-7} at 427°C , Calculate the enthalpy of the reaction ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

SOLUTION :**Formula used**

$$\log \frac{K_{p_2}}{K_{p_1}} = \frac{\Delta H}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Quantities given

$$K_{p_2} = 10^{-7}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$T_2 = 427 + 273 = 700 \text{ K}$$

$$K_{p_1} = 10^{-12}$$

$$T_1 = 327 + 273 = 600 \text{ K}$$

Substitution of values

$$\log \frac{10^{-7}}{10^{-12}} = \frac{\Delta H}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times \left[\frac{700 \text{ K} - 600 \text{ K}}{700 \text{ K} \times 600 \text{ K}} \right]$$

or

$$\begin{aligned}
 \Delta H &= \frac{\log 10^5 \times 2.303 \times 8.314 \text{ J} \times 600 \times 700}{100} \\
 &= 402089.98 \text{ J} \\
 &= \mathbf{402.08998 \text{ kJ}}
 \end{aligned}$$

SOLVED PROBLEM 12. For the dissociation of water

at 1773 K the value of K_p is $1.87 \times 10^{-6} \text{ atm}$. Assuming ideal behaviour of gases, Calculate the value of K_c

SOLUTION :**Formula used**

$$K_p = K_c (RT)^{\Delta n}$$

or
$$K_c = \frac{K_p}{(RT)^{\Delta n}}$$

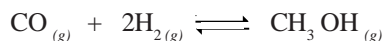
Quantities given

$$K_p = 1.87 \times 10^{-6} \text{ atm} \quad R = 0.082 \text{ atm lit K}^{-1} \text{ mol}^{-1} \quad T = 1773 \text{ K}$$

$$\Delta n = n_p - n_R = 1\frac{1}{2} - 1 = \frac{1}{2}$$

Substitution of values

$$\begin{aligned} K_c &= \frac{1.87 \times 10^{-6}}{(0.082 \times 1773)^{1/2}} \\ &= \frac{1.87 \times 10^{-6}}{12.0576} \\ &= 1.55 \times 10^{-7} \end{aligned}$$

SOLVED PROBLEM 13. For the reaction

hydrogen gas introduced into a five litre flask at 327 °C containing 0.2 mole of CO_(g) and a catalyst, until the pressure is 4.92 atm. At this point 0.1 mole of CH₃OH_(g) is formed. Calculate the equilibrium constant K_p and K_c .

SOLUTION :**(i) To calculate the total number of moles of all gas at equilibrium****Formula used**

$$PV = nRT \quad \text{or} \quad n = \frac{PV}{RT}$$

Quantities given

$$P = 4.92 \text{ atm} \quad V = 5 \text{ litres} \quad R = 0.082 \text{ atm lit K}^{-1} \text{ mol}^{-1}$$

$$T = 327 + 273 = 600\text{K.}$$

Substitution of values

$$\begin{aligned} n &= \frac{4.92 \text{ atm} \times 5 \text{ lit}}{0.082 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 600 \text{ K}} \\ &= 0.5 \text{ mole} \end{aligned}$$

(ii) To calculate the value of K_c **Formula used**

$$K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2}$$

Quantities given

$$\begin{aligned} \text{No. of moles of CH}_3\text{OH} &= 0.1 & \therefore [\text{CH}_3\text{OH}] &= \frac{0.1}{5} = 0.02 \text{ mol lit}^{-1} \\ \text{No. of moles of CO} &= 0.1 & \therefore [\text{CO}] &= \frac{0.1}{5} = 0.02 \text{ mol lit}^{-1} \\ \text{No. of moles of H}_2 &= 0.5 - (0.1 + 0.1) \\ &= 0.3 & \therefore [\text{H}_2] &= \frac{0.3}{5} = 0.06 \text{ mol lit}^{-1} \end{aligned}$$

Substitution of values

$$\begin{aligned} K_c &= \frac{0.02 \text{ mol lit}^{-1}}{0.02 \text{ mol lit}^{-1} \times (0.06 \text{ mol lit}^{-1})^2} \\ &= 277.78 \text{ mol}^{-2} \text{ lit}^2 \end{aligned}$$

(iii) To calculate the value of K_p

Formula used

$$K_p = K_c \times (RT)^{\Delta n}$$

Quantities given

$$K_c = 277.78$$

$$T = 600\text{K}$$

$$R = 0.082 \text{ atm lit K}^{-1} \text{ mol}^{-1}$$

$$\Delta n = n_p - n_R = 1 - 3 = -2$$

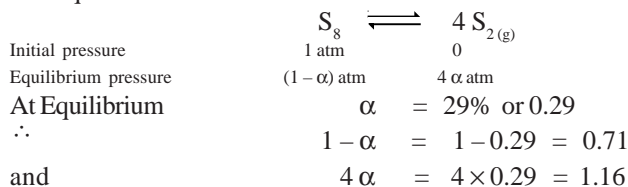
Substitution of values

$$\begin{aligned} K_p &= 277.78 \text{ mol}^{-2} \text{ lit}^{-1} \times (0.082 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 600 \text{ K})^{-2} \\ &= 277.78 \times (49.2 \text{ atm})^{-2} \\ &= \mathbf{0.11475 \text{ atm}^{-2}} \end{aligned}$$

SOLVED PROBLEM 14. When sulphur in the form of S_8 is heated at 900 K the initial pressure of 1 atm falls by 29% at equilibrium. This is because of conversion of some S_8 to S_2 . Find the value of equilibrium constant for the reaction.

SOLUTION :

The equilibrium reaction is



Formula used

$$K_p = \frac{p_{\text{S}_2}^4}{p_{\text{S}_8}} = \frac{(4\alpha)^4}{1 - \alpha}$$

Quantities given

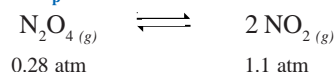
$$4\alpha = 1.16 \text{ atm}$$

$$1 - \alpha = 0.71 \text{ atm}$$

Substitution of values

$$\begin{aligned} K_p &= \frac{(1.16 \text{ atm})^2}{0.71 \text{ atm}} = \frac{1.3456}{0.71} \\ &= \mathbf{1.8952 \text{ atm}} \end{aligned}$$

SOLVED PROBLEM 15. An equilibrium mixture at 300 K contains N_2O_4 and NO_2 at 0.28 and 1.1 atm pressure respectively. If the volume of the container is doubled, calculate the new equilibrium pressure of the two gases.

SOLUTION :(i) To calculate the value K_p 

Formula used

$$K_p = \frac{p_{\text{NO}_2}^2}{p_{\text{N}_2\text{O}_4}}$$

Quantities given

$$p_{\text{NO}_2} = 1.1 \text{ atm}$$

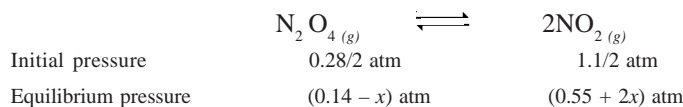
$$p_{\text{N}_2\text{O}_4} = 0.28 \text{ atm}$$

Substitution of values

$$K_p = \frac{(1.1 \text{ atm})^2}{0.28 \text{ atm}} = 4.32 \text{ atm}$$

(ii) To calculate the new equilibrium pressures when volume is doubled

When volume is doubled the pressure reduces to one half we have

**Formula used**

$$K_p = \frac{p_{\text{NO}_2}^2}{p_{\text{N}_2\text{O}_4}}$$

Quantities given

$$p_{\text{NO}_2} = (0.55 + 2x) \text{ atm}$$

$$p_{\text{N}_2\text{O}_4} = (0.14 - x) \text{ atm}$$

$$K_p = 4.32 \text{ atm}$$

Substitution of values

$$4.32 \text{ atm} = \frac{(0.55 + 2x)^2 \text{ atm}^2}{(0.14 - x) \text{ atm}}$$

$$\text{or} \quad 4x^2 + 2.2x + 0.3025 = 0.6048 - 4.32x$$

$$\text{or} \quad 4x^2 + 6.52x - 0.3023 = 0$$

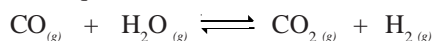
$$\text{or} \quad x = \frac{-6.52 \pm \sqrt{42.510 + 4.837}}{8} \quad \left[x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \right]$$

$$= \frac{-6.52 \pm 6.88}{8}$$

$$= 0.045 \text{ or } -1.675$$

$$\therefore p_{\text{NO}_2} = 0.55 + 2 \times 0.045 = \mathbf{0.64 \text{ atm}} \quad (\text{Rejecting } -1.675)$$

$$\text{and} \quad p_{\text{N}_2\text{O}_4} = 0.14x = \mathbf{0.095 \text{ atm}}$$

SOLVED PROBLEM 16. The equilibrium constant for the reaction

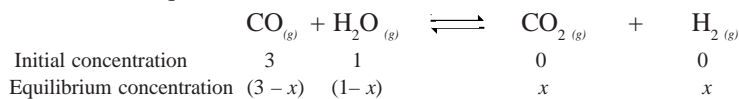
is 0.63. A mixture of 1 mole of water vapour and 3 moles of CO is allowed to come to equilibrium at a total pressure of 2 atmospheres. Calculate

(i) the no. of moles of hydrogen present at equilibrium

(ii) the partial pressure of each gas in the equilibrium mixture.

SOLUTION :**(i) To calculate the no. of moles of hydrogen at equilibrium**

The reaction equilibrium is



$$\begin{aligned} \text{Total number of moles at equilibrium} &= (3 - x) + (1 - x) + x + x \\ &= (3 + 1) \end{aligned}$$

Formula used

$$K_p = \frac{[\text{CO}_2][\text{H}_2]}{[\text{CO}][\text{H}_2\text{O}]}$$

Quantities given

$$K_p = 0.63$$

$$[\text{CO}] = 3 - x$$

$$[\text{H}_2\text{O}] = 1 - x$$

Substitution of values

$$0.63 = \frac{x \times x}{3-x \times 1-x}$$

$$\text{or } 0.63 \times (x^2 - 4x + 3) = x^2$$

$$\text{or } 0.373x^2 + 2.52x - 1.89 = 0$$

$$\text{or } x = 0.68$$

Thus the no. of moles of hydrogen at equilibrium = **0.68****(ii) To calculate the partial pressure of each gas****Formula used**

$$\text{Partial pressure} = \frac{\text{No. of moles of the gas}}{\text{Total no. of moles}} \times \text{Total pressure}$$

Quantities given

$$\text{Total pressure} = 2 \text{ atm}$$

$$\text{Total no. of moles} = 4$$

Substitution of values

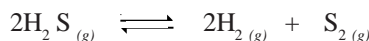
$$p_{\text{CO}_2} = \frac{x \times 2 \text{ atm}}{4} = \frac{0.68 \times 2 \text{ atm}}{4} = \mathbf{0.34 \text{ atm}}$$

$$p_{\text{H}_2} = \frac{x \times 2 \text{ atm}}{4} = \frac{0.68 \times 2 \text{ atm}}{4} = \mathbf{0.34 \text{ atm}}$$

$$p_{\text{CO}} = \frac{(3-x) \times 2 \text{ atm}}{4} = \frac{2.32 \times 2 \text{ atm}}{4} = \mathbf{1.16 \text{ atm}}$$

$$p_{\text{H}_2\text{O}} = \frac{(1-x) \times 2 \text{ atm}}{4} = \frac{0.32 \times 2 \text{ atm}}{4} = \mathbf{0.16 \text{ atm}}$$

SOLVED PROBLEM 17. Calculate the percent dissociation of $\text{H}_2\text{S}_{(g)}$ if 0.1 mole of H_2S is kept in 0.4 litre vessel at 1000 K. For the reaction.

the value of K_c is 1.0×10^{-6} .**SOLUTION :**

The chemical equation representing the equilibrium is

	$2\text{H}_2\text{S}_{(g)}$	\rightleftharpoons	$2\text{H}_{2(g)}$	+	$\text{S}_{2(g)}$
Initial concentration	0.1		0		0
Equilibrium concentration	$0.1 - x$		x		$x/2$
Molar Concentrations	$\frac{0.1 - x}{V}$		$\frac{x}{V}$		$\frac{x}{2V}$

Formula used

$$K_c = \frac{[\text{H}_2]^2 [\text{S}_2]}{[\text{H}_2\text{S}]^2}$$

Quantities given

$$K_c = 1.0 \times 10^{-6}$$

$$[\text{H}_2] = \frac{x}{V}$$

$$[\text{S}_2] = \frac{x}{2V}$$

$$[\text{H}_2\text{S}] = \frac{0.1 - x}{V} \text{ where } V = 0.4 \text{ litre}$$

Substitution of values

$$1.0 \times 10^{-6} = \frac{\left(\frac{x}{V}\right)^2 \left(\frac{x}{2V}\right)}{\left(\frac{0.1 - x}{V}\right)^2}$$

$$\begin{aligned}
 \text{or} \quad 1.0 \times 10^{-6} &= \frac{x^3}{2V(0.1)^2} & [\because 0.1 - x \approx 0.1] \\
 \text{or} \quad x^3 &= 2 \times 0.4 \times 0.01 \times 1.0 \times 10^{-6} & [\because V = 0.4 \text{ litre}] \\
 \text{or} \quad x^3 &= 8 \times 10^{-9} \\
 x &= \sqrt[3]{8 \times 10^{-9}} \\
 &= 2 \times 10^{-3} \\
 &= 0.002 \\
 \% \text{ Dissociation} &= \frac{\text{Amt. dissociated}}{\text{Initial concentration}} \times 100 \\
 &= \frac{0.002}{0.1} \times 100 \\
 &= 2\%
 \end{aligned}$$

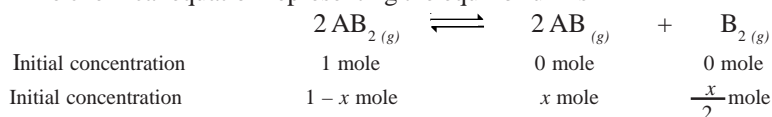
SOLVED PROBLEM 18. At temperature T, a compound AB_2 dissociates according to the reaction



with a degree of dissociation, x , which is small compared with unity. Deduce the expression for x in terms of the equilibrium constant, K_p , and the total pressure P.

SOLUTION :

The chemical equation representing the equilibrium is



$$\begin{aligned}
 \text{Total number of moles at equilibrium} &= (1 - x) + x + \frac{x}{2} \\
 &= 1 + \frac{x}{2} = \frac{2 + x}{2}
 \end{aligned}$$

(i) To deduce the expression for the total Pressure

Formula used

$$\text{Partial pressure} = \frac{\text{No. of moles of the gas}}{\text{Total no. of moles}} \times \text{Total Pressure}$$

Substitution of values

$$p_{\text{AB}_2} = \frac{1 - x}{\frac{2 + x}{2}} \times p = \frac{2(1 - x)}{2 + x} p$$

$$p_{\text{AB}} = \frac{x}{\frac{2 + x}{2}} \times p = \frac{2x}{2 + x} p$$

$$p_{\text{B}_2} = \frac{\frac{x}{2}}{\frac{2 + x}{2}} \times p = \frac{x}{2 + x} p$$

$$\begin{aligned}
 \text{Total pressure} &= p_{\text{AB}_2} + p_{\text{AB}} + p_{\text{B}_2} \\
 &= \frac{2(1 - x)}{2 + x} p + \frac{2x}{2 + x} p + \frac{x}{2 + x} p \\
 &= \frac{1}{2 + x} [1 - x + 2x + x] p
 \end{aligned}$$

$$= \frac{1-x}{2+x} + p$$

(ii) To deduce the expression for K_p

Formula used

$$K_p = \frac{p_{AB}^2 \times p_{B_2}}{p_{AB_2}^2}$$

Substitution of values

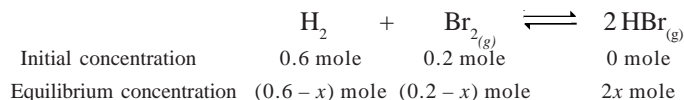
$$K_p = \frac{\left(\frac{2x}{2+x}p\right)^2 \left(\frac{2}{2+x}p\right)}{\left[\frac{2(1-x)}{2+x}\right]^2}$$

$$= \frac{x^3 p}{(2+x)(1-x)^2}$$

SOLVED PROBLEM 19. At 700 K, hydrogen and bromine react to form hydrogen bromide. The value of equilibrium constant for this reaction is 5×10^8 . Calculate the amount of H_2 , Br_2 and HBr at equilibrium if a mixture of 0.6 mole of H_2 and 0.2 mole of Br_2 is heated to 700 K.

SOLUTION :

The chemical equation representing the chemical equilibrium is



Formula used

$$K_c = \frac{[HBr]^2}{[H_2][Br_2]}$$

Quantities given

$$K_c = 5 \times 10^8$$

$$[HBr]^2 = 2x \text{ mole}$$

$$K_c = 5 \times 10^8$$

$$[Br_2] = (0.2 - x) \text{ mole}$$

Substituting of values

$$5 \times 10^8 = \frac{(2x \text{ mole})^2}{(0.6 - x \text{ mole})(0.2 - x \text{ mole})}$$

$$x = 0.6 \text{ mole or } 0.2 \text{ mole}$$

Rejecting the value 0.6 mole since it can not be greater than the initial concentration (= 0.2 mole)

Thus

$$[H_2] = 0.6 \text{ mole} - 0.2 \text{ mole} = 0.4 \text{ mole}$$

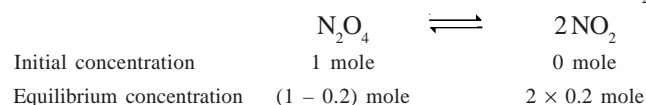
$$[Br_2] = 0.2 \text{ mole} - 0.2 \text{ mole} = 0 \text{ mole}$$

$$[HBr] = 2 \times 0.2 \text{ mole} = 0.4 \text{ mole}$$

SOLVED PROBLEM 20. 20% of N_2O_4 molecules are dissociated in a sample of gas at $27^\circ C$ and 760 torr. Calculate the density of the equilibrium mixture.

SOLUTION :

The chemical equation representing the decomposition of N_2O_4 is



$$\begin{aligned}
 \text{Total no. of moles at equilibrium} &= (1 - 0.2) \text{ mole} + 2 \times 0.2 \text{ mole} \\
 &= 0.8 \text{ mole} + 0.4 \text{ mole} \\
 &= 1.2 \text{ mole}
 \end{aligned}$$

Formula used

$$P V = n R T \quad \text{or} \quad V = \frac{n R T}{P}$$

Quantities given

$$n = 1.2 \text{ mole}$$

$$T = 27 + 273 = 300 \text{ K}$$

$$R = 0.082 \text{ atm lit K}^{-1} \text{ mol}^{-1}$$

$$P = 760 \text{ torr} = 1 \text{ atm}$$

Substitution of values

$$\begin{aligned}
 V &= \frac{1.2 \text{ mole} \times 0.082 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 300 \text{ K}}{1 \text{ atm}} \\
 &= 29.52 \text{ lit}
 \end{aligned}$$

To calculate the density

Formula used

$$\text{Density} = \frac{\text{Molecular mass}}{\text{Volume}}$$

Quantities given

$$\text{Molar mass of } N_2O_4 = 92 \text{ g}$$

$$V = 29.52 \text{ lit}$$

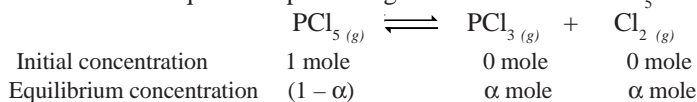
Substitution of values

$$\begin{aligned}
 \text{Density} &= \frac{92 \text{ g}}{29.52 \text{ lit}} \\
 &= 3.116 \text{ g lit}^{-1}
 \end{aligned}$$

SOLVED PROBLEM 21. At some temperature and under a pressure of 4 atm, PCl_5 is 10% dissociated. Calculate the pressure at which PCl_5 will be 20% dissociated, temperature remaining the same.

SOLUTION :

The chemical equation representing the dissociation of PCl_5



$$\begin{aligned}
 \text{Total number of moles at equilibrium} &= 1 - \alpha + \alpha + \alpha \text{ moles} \\
 &= 1 + \alpha \text{ moles}
 \end{aligned}$$

(i) To calculate the value of K_p

Formula used

$$K_p = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}}$$

Quantities given

$$\begin{aligned}
 P_{PCl_3} &= \frac{\alpha}{1 + \alpha} P & P_{Cl_2} &= \frac{\alpha}{1 + \alpha} P \\
 P_{PCl_5} &= \frac{1 - \alpha}{1 + \alpha} P & \text{where } P &= 4 \text{ atm and } \alpha = 0.1
 \end{aligned}$$

Substitution of values

$$K_p = \frac{\frac{\alpha}{1 + \alpha} P \times \frac{\alpha}{1 + \alpha} P}{\frac{1 - \alpha}{1 + \alpha} P}$$

$$\begin{aligned}
 K_p &= \frac{\alpha^2 P}{1 - \alpha^2} \\
 &= \frac{(0.1)^2 \times 4 \text{ atm}}{1 - 0.1^2} \\
 &= \frac{0.01 \times 4 \text{ atm}}{1 - 0.01} = \frac{0.04}{0.99} \text{ atm} = 0.040 \text{ atm}
 \end{aligned}$$

(ii) To calculate the pressure when $\alpha = 0.2$

Formula used

$$K_p = \frac{\alpha^2 p}{1 - \alpha^2}$$

Quantities given

$$K_p = 0.04 \text{ atm}$$

$$\alpha = 0.2$$

Substitution of values

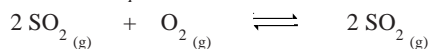
$$\begin{aligned}
 0.04 \text{ atm} &= \frac{0.2^2 \times 0.2 \times P'}{1 - (0.2)^2} \\
 &= \frac{0.04 \times P'}{1 - 0.04}
 \end{aligned}$$

or

$$P' = \frac{0.04 \times 0.096}{0.04} \text{ atm} = \mathbf{0.96 \text{ atm}}$$

ADDITIONAL PRACTICE PROBLEMS

1. The equilibrium constant K_p of the reaction



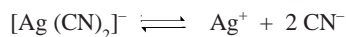
is 900 atm at 800 K. A mixture containing SO_3 and O_2 having initial partial pressures of 1 and 2 atm respectively is heated at constant volume to equilibrate. Calculate the partial pressure of each gas at 800 K.

Answer. 0.023 atm; 2.0115 atm; 0.977 atm

2. N_2O_4 is 25% dissociated at 37 °C and 1 atm pressure. Calculate (i) K_p and (ii) the percentage dissociation at 0.1 atm and 37 °C.

Answer. 2.66×10^{-1} atm; 63.2%

3. For the reaction



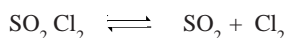
the equilibrium constant at 25 °C is 4.0×10^{-19} . Calculate the equilibrium concentration in a solution which was originally 0.1 molar in KCN and 0.03 molar in AgNO_3

Answer. 7.5×10^{-18} M

4. One mole of H_2 , two moles of I_2 and three moles of HI are injected in 1 litre flask. What will be the concentration of H_2 , I_2 and HI at equilibrium at 490 °C? The equilibrium constant for the reaction at 490 °C is 45.9.

Answer. 0.316 mol lit^{-1} ; 1.316 mol lit^{-1} ; 4.368 mol lit^{-1}

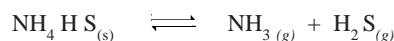
5. Find K_p for the following reaction



when the degree of dissociation is 63% at 78 °C and total pressure is 1 atm.

Answer. 0.656 atm

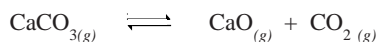
6. Calculate the equilibrium constant K_p for the reaction



when the total pressure of the mixture is 10 atm.

Answer. 25 atm

7. A sample of $\text{CaCO}_3_{(s)}$ is introduced into a sealed container of volume 0.500 litre and heated to 800 K until equilibrium is reached. The equilibrium constant for the reaction



is 3.9×10^{-2} atm at this temperature. Calculate the mass of CaO present at equilibrium.

Answer. 2.97×10^{-4} mol or 0.0166 g

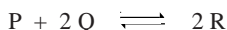
8. Determine the value of K_p for the following reaction



The value of K_c is 23.2 at 327 °C.

Answer. 23.2

9. Determine the value of equilibrium constant for the reaction



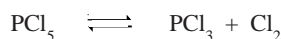
if 1.0 mol of P and 1.5 mol of Q are placed in 2.0 litre container and allowed to come to equilibrium. The equilibrium concentration of R is 0.35 mol lit⁻¹.

Answer. 2.36 mol lit⁻¹

10. At 25 °C and 1 atm pressure the partial pressure in an equilibrium mixture of N_2O_4 and NO_2 are 0.7 and 0.3 atm respectively. Calculate the partial pressures of these gases when they are in equilibrium at 25 °C and a total pressure of 5 atm.

Answer. 4.47 atm and 0.53 atm

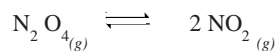
11. PCl_5 dissociates according to the equation



The density of the gas mixture at 473 K and 523 K is 70.2 and 57.9 respectively. Calculate the percentage dissociation of PCl_5 at these temperatures.

Answer. 48.5% and 80%

12. Calculate the value of K_c for the following reaction



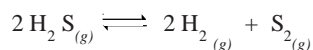
when K_p is 0.113 atm at 25 °C.

Answer. 4.624×10^{-3} mol lit⁻¹

13. Alcohol and acetic acid were mixed in equimolar proportions in aqueous medium at room temperature. At equilibrium 50% alcohol is converted into ester. Calculate how much ester will be formed if 2 moles of acetic acid and 1 mole of alcohol were mixed.

Answer. 0.67 mole]

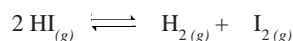
14. Calculate the percentage dissociation of H_2S if 1.0 mole of H_2S is introduced into 1.1 litre vessel at 1000 °C. The value of K_c for the reaction



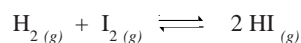
is 1.0×10^{-6} .

Answer. 1.3

15. The equilibrium constant K_p for the equation

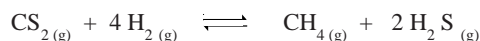


at 425 °C is 1.84. What is the value of K_c for the following equation?



Answer. 0.543

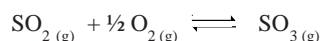
16. The value of K_c for the following reaction at 1173K is 0.28.



Calculate the value of K_p at this temperature.

Answer. 3×10^{-5}

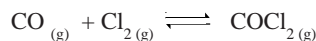
17. The reaction



has K_c equal to 56.30 at 627 °C. What is the value of K_p at this temperature?

Answer. 6.55

18. Phosgene, COCl_2 , is prepared according to the equation



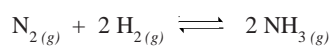
An equilibrium mixture at 395 °C contains 0.012 mole of CO and 0.025 mole of Cl_2 per litre as well as COCl_2 . if the value of K_c at 395 °C is 1.23×10^3 .

Answer. 0.37 m

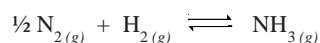
19. At 27 °C and 1 atm pressure N_2O_4 is 20% dissociated in the NO_2 . Calculate the value of K_p under these conditions.

Answer. 0.17 atm

20. One mole of nitrogen is mixed with three moles of hydrogen in a 4 litre container. If 0.0025 mole of nitrogen is converted to ammonia by the following reaction :



Calculate the equilibrium constant K_c for the reaction :



Answer. $3.82 \times 10^{-3} \text{ lit mol}^{-1}$

18

Distribution Law

CHAPTER

KEY CONCEPTS AND EQUATIONS



NERNST'S DISTRIBUTION LAW

If a solute X distributes itself between two non-miscible solvents A and B at constant temperature and X is in the same molecular condition in both solvents, then

$$\frac{\text{Concentration of } X \text{ in solvent } A}{\text{Concentration of } X \text{ in solvent } B} = K_D \text{ or } K$$

where K_D or K is the Distribution coefficient or Partition coefficient.

MODIFICATION OF NERNST DISTRIBUTION LAW

Case I. When solute undergoes Association

Let the solute X present in solvent A as simple molecules and in solvent B association of n molecules of X takes place to form X_n . Then, we have

$$\frac{C_1}{\sqrt[n]{C_2}} = K$$

when association occurs in solvent B .

Case II. When solute undergoes dissociation

Let the solute X be present in solvent A as simple molecules and in solvent B it dissociates to Y and Z and the degree of dissociation is α . Then we have

$$\frac{C_1}{C_2(1-\alpha)} = K$$

when dissociation occurs in solvent B .

HENRY'S LAW

At a constant temperature the solubility of a gas in a liquid is proportional to the pressure of the gas above it. *i.e.*

$$C = k \times P$$

where C is solubility or concentration, k is a constant and P is the pressure of the gas, k is called Henry's constant.

EXTRACTION WITH A SOLVENT

The removal of an organic substance from an aqueous solution is done by shaking the aqueous solution with a non-miscible organic solvent. After some time the aqueous and organic solvent layers separate in the funnel when most of the organic substance passes into the organic layer. It has been found that multistep extraction is more efficient than single step extraction as the amount of solute recovered is $2/3 A$ in a single step extraction as compared to $3/4 A$ in multistep extraction.

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. Succinic acid was shaken with a mixture of water and ether. The concentration of acid in two layers are as follows per 100 of the solution :

Concentration in water layer (C_w)	25.4	33.2	42.6
Concentration in ether layer (C_E)	4.2	5.5	7.1

Find out the partition coefficient. If succinic acid has normal molecular mass 118 in water, find its molecular mass in ether.

SOLUTION :**Formula used**

$$\text{Partition coefficient, } K = \frac{C_w}{C_E}$$

Quantities given

$C_w = 25.4$	33.2	42.6
$C_E = 4.2$	5.5	7.1

Substitution of values

$$K = \frac{25.4}{4.2} = 6.05 \quad K = \frac{33.2}{5.5} = 6.05 \quad K = \frac{42.6}{7.1} = 6.0$$

$$\text{Average value} = 6.02$$

Since the values of K are almost equal, molecular mass of succinic acid in ether will be the same as in water i.e. **118**.

SOLVED PROBLEM 2. 12 g of an organic substance A is present in 100 g of its aqueous solution. How much of it would be left behind after extracting the solution with two successive applications of 50 ml each of ether ? The distribution coefficient of A between water and ether is 2 in favour of ether.

SOLUTION :**Formula used**

$$K = \frac{C_E}{C_w} = \frac{x_I / 50}{(A - x_I) / 100} \quad \text{for the first step}$$

Quantities given

$$K = 2 \quad A = 12 \text{ g}$$

Substitution of values

$$2 = \frac{x_I / 50}{(12 - x_I) / 100}$$

$$2 = \frac{2 x_I}{12 - x_I}$$

or

$$12 - x_I = x_I$$

or

$$x_I = 6 \text{ g}$$

Now Amount left, $A_1 = 12 \text{ g} - 6 \text{ g} = 6 \text{ g}$

Again using the formula
$$K = \frac{x_2 / 50}{(A_1 - x_2) / 100}$$

Quantities given

$$K = 2$$

$$A_1 = 6 \text{ g}$$

Substitution of values

$$2 = \frac{x_2 / 50}{(6 - x_2) / 100} = \frac{2 x_2}{6 - x_2}$$

or

$$6 - x_2 = x_2$$

or

$$x_2 = 3 \text{ g}$$

The total amount of succinic acid extracted = $6 \text{ g} + 3 \text{ g} = 9 \text{ g}$

\therefore the amount of succinic acid left = $12 \text{ g} - 9 \text{ g} = \mathbf{3 \text{ g}}$

SOLVED PROBLEM 3. If the distribution coefficient of benzoic acid between water and benzene is 3.304 at 20°C , calculate the number of moles of benzoic acid which may be extracted from 100 ml of 0.2 molar aqueous solution by 10 ml of benzene.

SOLUTION :

Formula used

$$K = \frac{C_{\text{benzene}}}{C_{\text{water}}} = \frac{x/V}{(A-x)/v}$$

Quantities given

$$K = 3.304$$

$$V = 10 \text{ ml}$$

$$v = 100 \text{ ml}$$

$$A - x = 0.2 \text{ mole}$$

Substitution of values

$$3.304 = \frac{\frac{x}{10}}{\frac{0.2}{100}}$$

or

$$\frac{x}{10} \times \frac{100}{0.2} = 3.304$$

or

$$\frac{10x}{0.2} = 3.304$$

or

$$x = \frac{0.6608}{10} = \mathbf{0.0668 \text{ mole}}$$

SOLVED PROBLEM 4. Benzoic acid was shaken between benzene and water. From the following concentrations of the acid in grams in 10 ml of the aqueous and benzene layers, show that acid exists in benzene as $(\text{C}_6\text{H}_5\text{COOH})_2$

Acid in H_2O layer	0.150	0.195	0.289
Acid in Benzene layer	0.242	0.412	0.970

SOLUTION :

Formula used

$$K = \frac{C_1}{\sqrt[n]{C_2}}$$

Quantities given

$$n = 2 \text{ (dimerisation)}$$

$$C_1 = 0.150 \qquad 0.195 \qquad 0.289$$

$$C_2 = 0.242 \qquad 0.412 \qquad 0.970$$

Substitution of values

$$K = \frac{0.150}{\sqrt[2]{0.242}} = 0.3061$$

$$K = \frac{0.195}{\sqrt[2]{0.412}} = 0.3047$$

$$K = \frac{0.289}{\sqrt[2]{0.970}} = 0.2934$$

Since the value of K is almost constant, benzoic acid exists as dimer in benzene.

SOLVED PROBLEM 5. The solubility of a substance is twice as great in ether as in water. Compare the quantities extracted from 100 cc of aqueous solution by

(i) 100 cc ether in single operation

(ii) 50 cc ether in two successive operations.

SOLUTION :**(i) Single step extraction****Formula used**

$$K = \frac{x/V}{(A-x)v}$$

Quantities gives

$$K = \frac{C_{\text{ether}}}{C_{\text{water}}} = 2$$

$$V = 100 \text{ ml}$$

$$v = 100 \text{ ml}$$

Substitution of values

$$2 = \frac{x/100}{(A-x)/100}$$

or

$$2(A-x) = x$$

or

$$x = A \frac{2}{3}$$

(ii) Two step extraction**Formula used**

$$K = \frac{x_1/V}{(A-x_1)/v} \text{ for first operation}$$

Quantities given

$$K = 2$$

$$V = 50 \text{ ml}$$

$$v = 100 \text{ ml}$$

Substitution of values

$$2 = \frac{x_1/50}{(A-x_1)/100}$$

or

$$2(A-x_1) = 2x_1$$

or

$$x_1 = A/2$$

Formula used

$$K = \frac{x_2 / V}{(A/2 - x_2) / v} \quad \text{for the second operation}$$

Quantities given

$$K = 2$$

$$V = 50 \text{ ml}$$

$$v = 100 \text{ ml}$$

Substitution of values

$$2 = \frac{x_2 / 50}{(A/2 - x_2) / 100}$$

or

$$2 = \frac{x_2}{50} \times \frac{100}{A/2 - x_2}$$

or

$$A/2 - x_2 = x_2$$

or

$$x_2 = A/4$$

Thus

$$\text{the total amount extracted} = A/2 + A/4 = \frac{3A}{4}$$

SOLVED PROBLEM 6. Nernst reported the following results for the distribution of acetic acid between water and CCl_4 .

Concentration of acetic in CCl_4 (moles/litre)	0.292	0.725	1.41
Concentration of acetic in H_2O (moles/litre)	4.87	7.98	10.70

Assume that acetic acid has its normal molecular mass in water, calculate its molecular mass in CCl_4 .

SOLUTION :**Formula used**

$$K = \frac{C_{\text{CCl}_4}}{C_{\text{H}_2\text{O}}}$$

Quantities given

$C_{\text{CCl}_4} = 0.292$	0.725	1.41
$C_{\text{H}_2\text{O}} = 4.87$	7.98	10.70

Substitution of values

$$K = \frac{0.292}{4.87} = 0.05995 \quad K = \frac{0.725}{7.98} = 0.0909 \quad K = \frac{1.41}{10.70} = 0.1318$$

Since the values of K are not constant, acetic acid does not exist as monomer in CCl_4 . Now let us apply the formula

$$K = \frac{C_{\text{water}}}{\sqrt{C_{\text{CCl}_4}}}$$

Substitution of values

$$K = \frac{4.87}{\sqrt{0.292}} = 9.0185 \quad K = \frac{7.98}{\sqrt{0.725}} = 9.377 \quad K = \frac{10.70}{\sqrt{1.41}} = 9.014$$

Since the value of K is constant, acetic acid exists as dimer in CCl_4 and its

$$\text{molecular mass} = 2 \times \text{CH}_3\text{COOH} = 120$$

SOLVED PROBLEM 7. At 25°C the iodine solution in water which contains $0.0516 \text{ g lit}^{-1}$ is in equilibrium with CCl_4 solution containing $4.1280 \text{ g lit}^{-1}$ of iodine. If at 25°C iodine solutions contains 0.410 g lit^{-1} of iodine find out the solubility of iodine in CCl_4 solution.

SOLUTION :**(i) To calculate the distribution constant****Formula used**

$$K = \frac{C_{\text{water}}}{C_{\text{CCl}_4}}$$

Quantities given

$$C_{\text{water}} = 0.0516 \text{ g lit}^{-1}$$

$$C_{\text{CCl}_4} = 4.1280 \text{ g lit}^{-1}$$

Substitution of values

$$K = \frac{0.0516 \text{ g lit}^{-1}}{4.1280 \text{ g lit}^{-1}} = 0.0125$$

(ii) To calculate the solubility of I_2 in CCl_4 **Formula used**

$$\frac{\text{Conc. of } \text{I}_2 \text{ in water}}{\text{Conc. of } \text{I}_2 \text{ in } \text{CCl}_4} = K$$

Quantities given

$$K = 0.0125$$

$$\text{Conc. of } \text{I}_2 \text{ in water} = 0.410 \text{ g lit}^{-1}$$

Substitution of values

$$0.0125 = \frac{0.410 \text{ g lit}^{-1}}{\text{Conc. of } \text{I}_2 \text{ in } \text{CCl}_4}$$

or

$$\text{conc. of } \text{I}_2 \text{ in } \text{CCl}_4 = \frac{0.410}{0.0125} \text{ g lit}^{-1} = \mathbf{32.8 \text{ g lit}^{-1}}$$

SOLVED PROBLEM 8. If Henry's law constant for oxygen at 25°C is 3.30×10^{-7} mm Hg, find the solubility of oxygen in 1000 g of water at 25°C and a partial pressure of 190 mm Hg.

SOLUTION :**Formula used**

$$C = k \times P$$

Quantities given

$$k = 3.30 \times 10^{-7} \text{ mm}$$

$$P = 190 \text{ mm} = \frac{190}{760} \text{ atm} = 0.25 \text{ atm}$$

Substitution of values

$$C = 3.30 \times 10^{-7} \times 0.25 \text{ atm g lit}^{-1} \\ = \mathbf{0.825 \times 10^{-7} \text{ g lit}^{-1}}$$

SOLVED PROBLEM 9. Succinic acid was shaken with a mixture of water and ether. After distribution, upon analysis the concentrations of the acid in two layers are found as follows :

In aqueous layer (moles/lit)	0.0252	0.071	0.121
In ethereal layer (moles/lit)	0.0046	0.013	0.022

If succinic acid has similar molecular mass in ether and water, determine its partition coefficient.

SOLUTION :**Formula used**

$$K = \frac{C_{\text{Water}}}{C_{\text{ether}}}$$

Quantities given

C_{water}	= 0.0252	0.071	0.121
C_{ether}	= 0.0046	0.013	0.022

Substitution of values

$$K = \frac{0.0252}{0.0046} = 5.478$$

$$K = \frac{0.071}{0.013} = 5.4615$$

$$K = \frac{0.121}{0.022} = 5.50$$

Thus

average value of $K = 5.4798$

SOLVED PROBLEM 10. The following data have been obtained on the distribution of phenol between water and Chloroform

C_1	0.094	0.164	0.254	0.436
C_2	0.254	0.761	1.850	5.430

where C_1 is concentration in the aqueous layer and C_2 is the concentration in the Chloroform layer. What conclusions do you draw from these results regarding molecular condition of phenol in the chloroform solution ?

SOLUTION :**Formula used**

$$K = \frac{C_{\text{water}}}{\sqrt{C_{\text{CHCl}_3}}} \quad (\text{for association})$$

Quantities given

C_{water}	0.094	0.164	0.254	0.436
C_{CHCl_3}	0.254	0.761	1.850	5.430

Substitution of values

$$K = \frac{0.094}{\sqrt{0.254}} = 0.1865$$

$$K = \frac{0.164}{\sqrt{0.761}} = 0.1880$$

$$K = \frac{0.254}{\sqrt{1.850}} = 0.1868$$

$$K = \frac{0.436}{\sqrt{5.430}} = 0.1871$$

Since the values of K are constant, phenol exists as **dimer** in Chloroform.

SOLVED PROBLEM 11. The distribution coefficient of iodine between water and carbon disulphide is 0.0017. One litre of aqueous solution containing one gram of iodine is shaken with 100 ml of carbon disulphide till the equilibrium is reached. Find the amount of iodine extracted by carbon disulphide.

SOLUTION :**Formula used**

$$K = \frac{C_{\text{water}}}{C_{\text{CS}_2}}$$

Quantities given

$$K = 0.0017$$

$$C_{\text{water}} = 1 \text{ g lit}^{-1} = \frac{1}{1000} \text{ g ml}^{-1}$$

$$C_{\text{CS}_2} = \frac{x}{100} \text{ g ml}^{-1} \text{ where } x \text{ is the amt. of } I_2 \text{ extracted by 100 ml of } CS_2$$

Substitution of values

$$0.001 = \frac{\frac{1-x}{1000}}{\frac{x}{100}}$$

or

$$0.0017 = \frac{1-x}{1000} \times \frac{100}{x}$$

$$\begin{aligned} \text{or} \quad & \frac{1-x}{10x} = 0.0017 \\ \text{or} \quad & 1-x = 10x \times (0.0017) \\ & 1-x = 0.017x \\ \text{or} \quad & x = \frac{1}{1.017} = \mathbf{0.983 \text{ g}} \end{aligned}$$

SOLVED PROBLEM 12. At 298 K, an aqueous solution of iodine containing $0.0387 \times 10^{-3} \text{ kg dm}^{-3}$ of solution is in equilibrium with $3.31 \times 10^{-3} \text{ kg dm}^{-3}$ of iodine in carbon tetrachloride. If solubility of iodine in CCl_4 is $0.0291 \text{ kg dm}^{-3}$, what is the solubility of iodine in water?

SOLUTION :

Formula used

$$K = \frac{C_{\text{water}}}{C_{\text{CCl}_4}}$$

Quantities given

$$C_{\text{water}} = 0.0387 \times 10^{-3} \text{ kg dm}^{-3}$$

$$C_{\text{CCl}_4} = 3.31 \times 10^{-3} \text{ kg dm}^{-3}$$

Substitution of values

$$K = \frac{0.0387 \times 10^{-3} \text{ kg dm}^{-3}}{3.31 \times 10^{-3} \text{ kg dm}^{-3}} = 0.01169$$

Now using the formula

$$K = \frac{\text{Solubility of } I_2 \text{ in water}}{\text{Solubility of } I_2 \text{ in } \text{CCl}_4}$$

Quantities given

$$K = 0.01169$$

$$\text{Solubility of } I_2 \text{ in } \text{CCl}_4 = 0.0291 \text{ kg dm}^{-3}$$

Substitution of values

$$0.01169 = \frac{\text{Solubility of } I_2 \text{ in water}}{0.0291 \text{ kg dm}^{-3}}$$

$$\begin{aligned} \text{or} \quad \text{Solubility of } I_2 \text{ in water} &= 0.01169 \times 0.0291 \text{ kg dm}^{-3} \\ &= \mathbf{0.00034 \text{ kg dm}^{-3}} \end{aligned}$$

SOLVED PROBLEM 13. An organic acid was dissolved in two immiscible solvents (A) and (B). At equilibrium the concentration of the acid in (A) and (B) was found to be 0.40 and 0.64 mole lit^{-1} respectively. Calculate the distribution coefficient of the organic acid, if it forms dimer in the solvent B.

SOLUTION :

Formula used

$$K = \frac{C_A}{\sqrt{C_B}}$$

Quantities given

$$C_A = 0.40$$

$$C_B = 0.64$$

Substitution of values

$$K = \frac{0.40}{\sqrt{0.64}} = \frac{0.40}{0.8} = \mathbf{0.5}$$

SOLVED PROBLEM 14. An organic acid is distributed between 500 ml each of a solvent A and water. In water it is dissociated. The amount of acid in aqueous layer was 6 grams and in solvent A, it was 0.72 gram. If the distribution coefficient of the acid between the solvent A and water is 0.16, Calculate the degree of dissociation, assuming that the acid has normal molecular mass in A.

SOLUTION :**Formula used**

$$K = \frac{C_A}{C_{\text{water}} \times (1-x)} \quad \text{where } x \text{ is the degree of dissociation}$$

Quantities given

$$K = 0.16$$

$$C_{\text{water}} = 6 \text{ g}$$

$$C_A = 0.72 \text{ g}$$

Substitution of values

$$0.16 = \frac{0.72 \text{ g}}{6 \text{ g} \times (1-x)}$$

$$\text{or} \quad 0.96(1-x) = 0.72$$

$$\text{or} \quad 0.96 - 0.96x = 0.72$$

$$1-x = \frac{0.72}{0.96} = 0.75$$

$$\text{or} \quad x = 0.25 \quad \text{or} \quad 25\%$$

SOLVED PROBLEM 15. Acetic acid was shaken with water and CCl_4 and the following concentrations in g mol lit^{-1} were found in two layers :

Water layer	5.02	7.98	10.70
CCl_4 layer	0.292	0.725	1.41

Assuming that acetic acid has single molecule in water, show that it exists as double molecule in CCl_4 .

SOLUTION :**Formula used**

$$K = \frac{C_{\text{water}}}{\sqrt{C_{\text{CCl}_4}}}$$

Quantities given

$$C_{\text{water}} = 5.02$$

$$7.98$$

$$10.70$$

$$C_{\text{CCl}_4} = 0.292$$

$$0.725$$

$$1.41$$

Substitution of values

$$K = \frac{5.02}{\sqrt{0.292}} = 9.2296$$

$$K = \frac{7.98}{\sqrt{0.725}} = 9.3772$$

$$K = \frac{10.70}{\sqrt{1.41}} = 9.0143$$

Since the value of K is constant, acetic acid exists as **dimer** in CCl_4 .

SOLVED PROBLEM 16. A solid X is added to a mixture of benzene and water. After shaking well and allowing it to stand, 10 ml of benzene layer was found to contain 0.13 g of X , and 100 ml of water layer contained 0.22 g of X . Calculate the value of distribution coefficient.

SOLUTION :**Formula used**

$$K = \frac{C_{\text{benzene}}}{C_{\text{water}}}$$

Quantities given

$$C_{\text{benzene}} = \frac{0.13}{10} \text{ g ml}^{-1}$$

$$C_{\text{water}} = \frac{0.22}{100} \text{ g ml}^{-1}$$

Substitution of values

$$K = \frac{\frac{0.13}{10} \text{ g ml}^{-1}}{\frac{0.22}{100} \text{ g ml}^{-1}} = 5.9091$$

SOLVED PROBLEM 17. Calculate how much succinic acid would be extracted from 100 ml of water containing 5 g of acid if extracted with 50 ml of ether. Partition coefficient of succinic acid between water and ether is 5.5.

SOLUTION :**Formula used**

$$K = \frac{C_{\text{water}}}{C_{\text{ether}}}$$

Quantities given

$$K = 5.5$$

$$C_{\text{water}} = \frac{5 \text{ g}}{100 \text{ ml}} \quad C_{\text{ether}} = \frac{5 - x \text{ g}}{50 \text{ ml}}$$

Substitution of values

$$\begin{aligned} 5.5 &= \frac{\frac{5 \text{ g}}{100 \text{ ml}}}{\frac{5 - x \text{ g}}{50 \text{ ml}}} \\ 5.5 &= \frac{5}{100} \times \frac{50}{5 - x} \\ 11 \times (5 - x) &= 5 \\ 55 - 11x &= 5 \\ x &= \frac{55 - 5}{11} = 4.545 \text{ g} \end{aligned}$$

SOLVED PROBLEM 18. The partition coefficient of a substance between benzene and water is 10.1. How much substance will be extracted from its 250 ml aqueous solution containing 2.5 g of it by using 200 ml benzene in

- (i) two equal portions
- (ii) a single lot

SOLUTION :**(i) In a single lot****Formula used**

$$K = \frac{C_{\text{benzene}}}{C_{\text{water}}}$$

Quantities given

$$K = 10.1$$

$$C_{\text{Benzene}} = \frac{x \text{ g}}{200 \text{ ml}} \quad C_{\text{water}} = \frac{2.5 - x \text{ g}}{250 \text{ ml}}$$

Substitution of values

$$10.1 = \frac{\frac{x}{200} \text{ g ml}^{-1}}{\frac{2.5 - x}{250} \text{ g ml}^{-1}} = \frac{x}{200} \times \frac{250}{(2.5 - x)}$$

$$40.4 = \frac{5x}{2.5 - x}$$

or $5x = 101 - 40.4x$

or $x = 2.22 \text{ g}$

(ii) In two operations of 100 ml each

Let the amount extracted be x in 1st operation

Formula used

$$K = \frac{\frac{x_1}{100}}{\frac{2.5 - x_1}{250}}$$

Quantities given

$K = 10.1$

Substitution of values

$$10.1 = \frac{\frac{x_1}{100}}{\frac{2.5 - x_1}{250}} = \frac{x_1}{100} \times \frac{250}{2.5 - x_1}$$

$$20.2 = \frac{5x_1}{2.5 - x_1}$$

or $5x_1 = 50.5 - 20.2x_1$

or $x_1 = \frac{50.5}{25.2} = 2.0 \text{ g}$

Now Let the amount extracted be x_2 in 2nd operation

Formula used

$$K = \frac{\frac{x_2}{100}}{\frac{0.5 - x_2}{250}}$$

Quantities given

$K = 10.1$

Substitution of values

$$10.1 = \frac{\frac{x_2}{100}}{\frac{0.5 - x_2}{250}} = \frac{x_2}{100} \times \frac{250}{(0.5 - x_2)}$$

$$10.1 \times (1 - 2x_2) = 5x_2$$

$$10.1 - 20.2x_2 = 5x_2$$

or $x_2 = \frac{10.1}{25.2} = 0.4 \text{ g}$

Total amount extracted $= x_1 + x_2 = 2 \text{ g} + 0.4 \text{ g} = 2.4 \text{ g}$

SOLVED PROBLEM 19. Experiments in the study of rate of distribution of phenol between H_2O and chloroform gave the following results :

Concentration in aqueous solution	C_1	0.094	0.103	0.254
Concentration in Chloroform	C_2	0.254	0.761	1.850

Find whether phenol exists as monomer or dimer.

SOLUTION :

In case phenol exists as monomer the value of K obtained from the following formula should be constant

Formula used

$$K = \frac{C_{\text{water}}}{C_{\text{CHCl}_3}}$$

Quantities given

$$C_{\text{water}} = 0.094 \quad 0.103 \quad 0.254$$

$$C_{\text{CHCl}_3} = 0.254 \quad 0.761 \quad 1.850$$

Substitution of values

$$K = \frac{0.094}{0.254} = 0.3700 \quad K = \frac{0.103}{0.761} = 0.135 \quad K = \frac{0.254}{1.850} = 0.1373$$

Since the value of K is not constant, phenol does not exist as monomer.

Now

Formula used

$$K = \frac{C_{\text{water}}}{\sqrt{C_{\text{CHCl}_3}}}$$

Substitution of values

$$K = \frac{0.094}{\sqrt{0.254}} = 0.1865 \quad K = \frac{0.103}{\sqrt{0.761}} = 0.1868 \quad K = \frac{0.254}{\sqrt{1.850}} = 0.1867$$

Since the value of K is constant, phenol exists as **dimer** in chloroform.

SOLVED PROBLEM 20. An organic compound is twice more soluble in ether than in water. Calculate the amount of the compound extracted when 100 ml of aqueous solution containing 1 g of compound is shaken with (i) 100 ml of ether at one time (ii) two successive quantities of 50 ml each.

SOLUTION :

(i) In a single operation

Formula used

$$K = \frac{C_{\text{ether}}}{C_{\text{water}}}$$

Let x be the amt. of compound extracted by 100 ml of ether.

Quantities given

$$C_{\text{ether}} = \frac{x}{100} \text{ g ml}^{-1} \quad C_{\text{water}} = \frac{1-x}{100} \text{ g ml}^{-1} \quad K = 2$$

Substitution of values

$$2 = \frac{\frac{x}{100} \text{ g ml}^{-1}}{\frac{1-x}{100} \text{ g ml}^{-1}} = \frac{x}{1-x}$$

or

$$2(1-x) = x$$

or

$$3x = 2$$

$$x = \mathbf{0.67 \text{ g}}$$

(ii) In double operation

Let x_1 be the amount of the compound extracted by 50 ml of ether

Formula used

$$K = \frac{C_{ether}}{C_{water}}$$

Substitution of values

$$2 = \frac{\frac{x_1}{50} \text{ g ml}^{-1}}{\frac{1-x_1}{100} \text{ g ml}^{-1}} = \frac{x_1}{50} \times \frac{100}{1-x_1}$$

or

$$1 - x_1 = x_1$$

or

$$2x_1 = 1$$

$$x_1 = 0.5$$

$$\text{Amt. of the compound left} = 1.0 \text{ g} - 0.5 \text{ g} = 0.5 \text{ g}$$

Now in second operation let the amount extracted be x_2

Formula used

$$K = \frac{C_{ether}}{C_{water}}$$

Quantities given

$$K = 2$$

$$C_{ether} = \frac{x_2}{50} \text{ g ml}^{-1}$$

$$C_{water} = \frac{0.5}{100} \text{ g ml}^{-1}$$

Substitution of values

$$2 = \frac{\frac{x_2}{50} \text{ g ml}^{-1}}{\frac{0.5}{100} \text{ g ml}^{-1}} = \frac{x_2}{50} \times \frac{100}{0.5}$$

$$2 = \frac{2x_2}{0.5}$$

or

$$x_2 = \frac{1}{2} = 0.5$$

$$\text{Total amount extracted } 0.5 + 0.5 = 1 \text{ g}$$

SOLVED PROBLEM 21. At 298 K an aqueous solution of iodine containing $0.0516 \text{ g lit}^{-1}$ is in equilibrium with a carbon tetrachloride (CCl_4) solution containing 4.412 g lit^{-1} . The solubility of iodine in water at 298 K is 0.34 g lit^{-1} . Find the solution of iodine in carbon tetrachloride.

SOLUTION :**(i) To calculate the value of Distribution coefficient K****Formula used**

$$K = \frac{C_{\text{CCl}_4}}{C_{\text{water}}}$$

Quantities given

$$C_{\text{CCl}_4} = 4.412 \text{ g lit}^{-1}$$

$$C_{\text{water}} = 0.0516 \text{ g lit}^{-1}$$

Substitution of values

$$K = \frac{4.412 \text{ g lit}^{-1}}{0.0516 \text{ g lit}^{-1}} = 85.5$$

(ii) To calculate the solubility of iodine in CCl_4 .**Formula used**

$$K = \frac{\text{Solubility of Iodine in } \text{CCl}_4}{\text{Solubility of Iodine in water}}$$

Quantities given

$$\text{Solubility of Iodine in water} = 0.34 \text{ g lit}^{-1} \quad K = 85.5$$

Substitution of values

$$85.5 = \frac{\text{Solubility of Iodine in } \text{CCl}_4}{0.34 \text{ g lit}^{-1}}$$

$$\begin{aligned} \text{or} \quad \text{Solubility of Iodine in } \text{CCl}_4 &= 85.5 \times 0.34 \text{ g lit}^{-1} \\ &= \mathbf{29.07 \text{ g lit}^{-1}} \end{aligned}$$

SOLVED PROBLEM 22. The distribution constant of a certain solid X between two immiscible solvents A and B is 10 at 25 °C. If the solubility of the solid in solvent A is 4.8 mol lit⁻¹, what is the solubility in solvent B?

SOLUTION :**Formula used**

$$K = \frac{\text{Solubility in solvent A}}{\text{Solubility in solvent B}}$$

Quantities given

$$K = 10 \quad \text{Solubility in solvent A} = 4.8 \text{ mol lit}^{-1}$$

Substitution of values

$$\begin{aligned} 10 &= \frac{4.8 \text{ mol lit}^{-1}}{\text{Solubility in solvent B}} \\ \text{or} \quad \text{Solubility in solvent B} &= \frac{4.8 \text{ mol lit}^{-1}}{10} \\ &= \mathbf{0.48 \text{ mol lit}^{-1}} \end{aligned}$$

SOLVED PROBLEM 23. An organic acid is distributed between 200 cm³ each of a solvent A and water. In water it is dissociated. The amount of acid in aqueous layer was 2.4 g and in the solvent A layer it was 0.288 g. If the partition coefficient between the solvent A and water is 0.16, calculate the degree of dissociation assuming that the acid has normal molecular mass in solvent A.

SOLUTION :**Formula used**

$$K = \frac{C_1}{C_2(1 - \alpha)}$$

Quantities given

$$\begin{aligned} K &= 0.16 \\ C_1 &= 0.288 \text{ g}/200 \text{ cm}^3 = 1.44 \times 10^{-3} \text{ g cm}^{-3} \\ C_2 &= 2 \text{ g}/200 \text{ cm}^3 = 1.2 \times 10^{-2} \text{ g cm}^{-3} \end{aligned}$$

Substitution of values

$$0.16 = \frac{1.44 \times 10^{-3} \text{ g cm}^{-3}}{1.2 \times 10^{-2} \text{ g cm}^{-3} (1 - \alpha)}$$

$$\begin{aligned} \text{or} \quad (1 - \alpha) &= \frac{1.44}{1.2 \times 0.16} = 0.75 \\ \text{or} \quad \alpha &= 0.25 \text{ or } 25\% \end{aligned}$$

SOLVED PROBLEM 24. In the distribution of benzoic acid between water and benzene the following values have been obtained in equal volumes of solvents :

$C_{\text{water}} \text{ (g)}$	1.50	1.95	2.97
$C_{\text{Benzene}} \text{ (g)}$	24.2	41.2	97.0

What is the molecular condition of benzoic acid in benzene ?

SOLUTION :

Formula used

$$K = \frac{C_{\text{water}}}{C_{\text{benzene}}}$$

Quantities given

$C_{\text{water}} =$	1.5	1.95	2.97
$C_{\text{benzene}} =$	24.2	41.2	97.0

Substitution of values

$$K = \frac{1.5}{24.2} = 0.061983 \quad K = \frac{1.95}{41.2} = 0.04733 \quad K = \frac{2.97}{97.0} = 0.030619$$

Since the value of K is not constant, benzoic acid does not exist as monomer in benzene. Now

Formula used

$$K = \frac{C_{\text{water}}}{\sqrt{C_{\text{benzene}}}}$$

Substitution of values

$$\begin{aligned} K &= \frac{1.5}{\sqrt{24.2}} = \frac{1.5}{4.919} = 0.3049 \\ K &= \frac{1.95}{\sqrt{41.2}} = \frac{1.95}{6.4187} = 0.3038 \\ K &= \frac{2.97}{\sqrt{97.0}} = \frac{2.97}{9.8488} = 0.30156 \end{aligned}$$

Now the value of distribution coefficient is constant. Hence benzoic acid exists as dimer in benzoic acid.

SOLVED PROBLEM 25. Succinic acid shows molecular mass in water and is associated in benzene. The following data was obtained on the distribution of succinic acid between water and benzene.

C_{water}	0.150	0.195	0.289
C_{benzene}	2.42	4.120	9.700

Calculate the molecular mass of succinic acid in benzene

SOLUTION :

Formula used

$$K = \frac{C_{\text{water}}}{\sqrt{C_{\text{benzene}}}}$$

Quantities given

$C_{\text{water}} =$	0.150	0.195	0.289
$C_{\text{benzene}} =$	2.42	4.120	9.70

Substitution of values

$$K = \frac{0.150}{\sqrt{2.42}} = \frac{0.150}{1.5556} = 0.0964$$

$$K = \frac{0.195}{\sqrt{4.120}} = \frac{0.195}{2.0297} = 0.0960$$

$$K = \frac{0.289}{\sqrt{9.70}} = \frac{0.289}{3.11448} = 0.09279$$

Since the value of K is almost constant, succinic acid exists as dimer in benzene.

$$\begin{aligned}\therefore \text{mol. mass of succinic acid in benzene} &= 2 \times (\text{C}_4\text{H}_6\text{O}_4) \\ &= 2 \times 118 \\ &= \mathbf{236}\end{aligned}$$

ADDITIONAL PRACTICE PROBLEMS

1. Iodine was shaken in a mixture of CS_2 and water. The concentrations of I_2 in two layers are as follows :

Concentration of I_2 in CS_2 (g dm^{-3})	41	66	129	174
Concentrations of I_2 in water (g dm^{-3})	0.1	0.161	0.314	0.423

Calculate the distribution constant of I_2 between CS_2 and water.

Answer. 410

2. In an experiment on distribution of I_2 with CCl_4 and H_2O following results were obtained

Concentration of I_2 in CCl_4 layer ($\text{g}/100 \text{ cm}^{-3}$)	5.1	10.2	15.2	20.3
Concentration of I_2 in water H_2O ($\text{g}/100\text{cm}^{-3}$)	0.06	0.119	0.178	0.236

Calculate the distribution constant of I_2 between CCl_4 and water.

Answer. 85.5

3. A solid Y was added to mixture of benzene and water. After shaking well and allowing it to stand, 20 cm^3 of the benzene was found to contain 0.26 g of Y and 200 cm^3 of water layer contained 0.44 g of Y. Calculate the value of distribution constant.

Answer. 5.9

4. At 298 K an aqueous solution of iodine containing 0.0516 g dm^{-3} is in equilibrium with CHCl_3 solution containing 4.412 g dm^{-3} . The solubility of iodine in water at 298 K is 0.34 g dm^{-3} . Find out the solubility of iodine in CHCl_3 .

Answer. 29.07 g dm^{-3}

5. The solubility of iodine in water is 0.35 g lit^{-1} . Calculate its solubility in carbon tetrachloride, if the distribution constant of iodine in CCl_4 and water is 88.

Answer. 30.8 g lit^{-1}

6. In an experiment on distribution of succinic acid between water and ether at 20°C , 10 ml of ethereal layer contains 0.046 g of acid. Calculate the amount of succinic acid present in 25 ml of the aqueous solution in equilibrium with it if the distribution coefficient of succinic acid between water and ether is 5.2.

Answer. 0.598 g

7. Succinic acid shows normal molecular mass in water and abnormal in benzene. When succinic acid was distributed between water and benzene following results were obtained.

Concentration of succinic acid in Benzene (g lit^{-1})	1.50	1.95	2.89
Concentration of succinic acid in water (g lit^{-1})	24.70	41.20	96.50

Calculate the molecular mass of succinic acid in benzene.

Answer. 236

8. 100 g of an acid was dissolved in 1 litre of water. The distribution coefficient of acid between ether and water is 3. One litre of ether in one lot was used to extract acid. Calculate the amount of acid extracted.

Answer. 37.5

9. In an experiment of distribution of benzoic acid between water and benzene, following results were obtained:

Concentration in water (mol lit^{-1})	0.00579	0.00749	0.0114
Concentration in C_6H_6 (mol lit^{-1})	0.0485	0.0835	0.1950

Calculate the molecular mass of benzoic acid in benzene assuming that acid behaves normally in water.

Answer. 244

10. The distribution coefficient of an organic acid between benzene and water is 80. An aqueous solution of the acid containing 2.25 g in 100 cm^3 was extracted with (i) 10 cm^3 of benzene in one lot and (ii) twice with 5 cm^3 benzene each time. Calculate the amount of acid extracted in each experiment.

Answer. (i) 2 g (ii) 2.16 g

19

The Phase Rule

CHAPTER

KEY CONCEPTS AND EQUATIONS



THE PHASE RULE

It is an important generalisation dealing with the behaviour of heterogeneous systems. With its application it is possible to predict the effect of changing pressure, temperature and concentration on a heterogeneous system in equilibrium. The phase rule is

$$F = C - P + 2$$

or

$$F + P = C + 2$$

where F is the number of degrees of freedom, C is the number of components and P is the number of phases of the system. These terms are expressed in the following section.

PHASE, COMPONENT AND DEGREES OF FREEDOM

A **phase** may be defined as any homogeneous part of a system having all physical and chemical properties the same throughout.

A **component** may be defined as the least number of independent chemical constituents in terms of which the composition of every phase can be expressed by means of a chemical equation.

The **degree of freedom** is defined as the least number of variable factors (concentration, pressure and temperature) which must be specified so that the remaining variables are fixed automatically and the system is completely defined.

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. How many phases are present in each of the following system :

- (i) a drop of water placed in a stoppered bottle.
- (ii) a piece of molten ice placed in a beaker covered with a watch glass
- (iii) mixture of N_2 , H_2 and O_2 .

SOLUTION : (i) No. of phases in a drop of water in a stoppered bottle

There will be two phases viz. liquid water and its vapours.

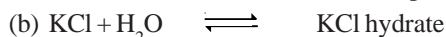
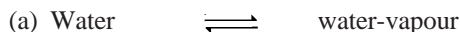
(ii) No. of phases in a piece of molten ice placed in a beaker covered with watch glass

There will be two phases in a piece of molten ice placed in a beaker covered with watch glass viz. liquid water and its vapours.

(iii) Mixture of N_2 , H_2 and O_2 .

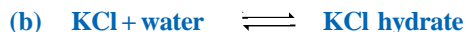
There will be only one phase in a mixture of N_2 , H_2 and O_2 .

SOLVED PROBLEM 2. How many components are present in the following systems ?



SOLUTION : (a) Water \rightleftharpoons water-vapour

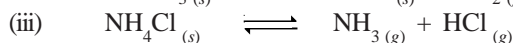
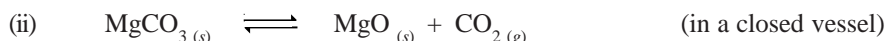
The system contains only one component as only one specie is chemically independent.



In this system there are only two components which are chemically independent.

SOLVED PROBLEM 3. Calculate the number of components in the following systems :

(i) a solution of common salt

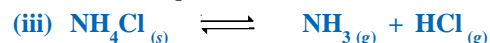


SOLUTION : (i) A solution of common salt

A solution of NaCl in water is a 1-phase system. Its composition can be expressed in terms of two chemical individuals – NaCl and water.

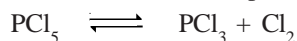


In this equilibrium the composition of all the phases can be expressed in terms of any two of three chemical substances in equilibrium. Thus the no. of components in the system is 2.

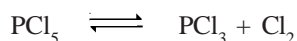


The composition of all the phases can be expressed in terms of the same chemical substances NH_4Cl . Thus the no. of components in the system is one.

SOLVED PROBLEM 4. Calculate the number of components in the equilibrium



SOLUTION : In the equilibrium

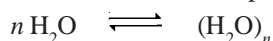


There are three species present. We can change the number of moles of any two of these chemical species as the no. of moles of third component is calculated by the equilibrium

$$K = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$

Thus there are only two components in this system.

SOLVED PROBLEM 5. Calculate the number of components in the equilibrium



SOLUTION : This system contains a number of chemical species : H_2O , $(\text{H}_2\text{O})_2$, $(\text{H}_2\text{O})_3, \dots$. But there is only one component because all the equilibria established in the system depend only on one chemically independent specie H_2O . Thus there is only one component in this system.

SOLVED PROBLEM 6. Calculate the number of phases (P), components (C) and degrees of freedom (F) for the system in which ammonium chloride is in equilibrium with ammonia and hydrochloric acid certain amount of hydrochloric acid initially present in the system.

SOLUTION :

In the given system no. of phases = 2

no. of components = 2

It is a two component system because the concentration of ammonia is not always equal to the concentration of HCl in the vapour phase

Applying phase rule

$$F + P = C + 2$$

or $F + 2 = 2 + 2$

or $F = 2$

SOLVED PROBLEM 7. The atmospheric pressure at a Hill station on particular day is 650 torr. At what temperature does water boil in the hill station on that day ? ($\Delta H_{\text{vap}} = 40.67 \text{ kJ mol}^{-1}$).

SOLUTION :

Formula used

$$\log \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}}{2.303 \times R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

Quantities given

$$T_1 = 273 + 100 = 373 \text{ K}$$

$$P_1 = 760 \text{ torr}$$

$$R = 8.314 \text{ J}$$

$$P_2 = 650 \text{ torr}$$

$$\Delta H_{\text{vap}} = 40.67 \text{ kJ mol}^{-1}$$

Substitution of values

$$\log \frac{650}{760} = \frac{40.67 \times 10^3}{2.303 \times 8.314} \left[\frac{1}{373} - \frac{1}{T_2} \right]$$

$$\log 0.8552 = 2124.077 \left[\frac{1}{373} - \frac{1}{T_2} \right]$$

or

$$\begin{aligned} T_2 &= 368.60 \text{ K} \\ &= 368.60 - 273 \\ &= 95.6^\circ \text{C} \end{aligned}$$

ADDITIONAL PRACTICE PROBLEMS

1. Starting with pure NH_4Cl the following equilibrium is established.



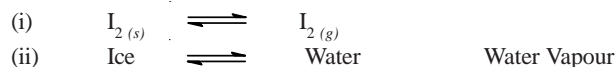
State the number of components in the system.

Answer. 2

2. Calculate the number of phases in a mixture of four gases enclosed in a container.

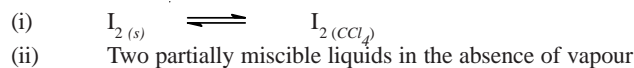
Answer. 1

3. State how many phases are present in the following systems



Answer. (i) 2, (ii) 3

4. How many degrees of freedom will be present in the following systems ?



Answer. (i) 2, (ii) 2

5. The vapour pressure of 2,2,4-trimethylpentane at 20.7 °C and 29.1°C are 40 and 60 torr respectively. Calculate the enthalpy of vaporization of this compound.
Answer. 35.6 kJ mol⁻¹
6. The atmospheric pressure in a deep valley on a particular day is 120 torr. Calculate the boiling point of water in that valley on that day (Heat of vaporization = 2.260 kJ g⁻¹).
Answer. 386.45 K
7. Determine the number of phases, components and degrees of freedom in the system : Ice, water and vapour in equilibrium.
Answer. 3,1 and 0
8. How many degrees of freedom will be present in a solution of sodium sulphate in equilibrium with water vapour ?
Answer. 2
9. Calculate the number of components present in the following systems
 (i) A solution of common salt
 (ii) NH_{3(g)}
Answer. (i) 2, (i) 1
10. Calculate the degrees of freedom and number of components for a system of sodium chloride solution in water containing undissolved salt, in equilibrium with water vapour.
Answer. 1 and 2

20

Chemical Kinetics

CHAPTER

KEY CONCEPTS AND EQUATIONS



RATE OF A REACTION

It is defined as the change in concentration of any of reactants or products per unit time. For the reaction



$$\text{Rate of reaction} = - \frac{d[A]}{dt} = \frac{d[B]}{dt}$$

The negative sign indicates that the concentration of reactant A is decreasing with time.

UNITS OF RATE

Reaction rate has the units of concentration divided by time. Concentration is expressed in moles per litre and time in seconds, minutes, hours or years. Thus,

$$\text{Units of reaction rate are mole lit}^{-1} \text{ sec}^{-1} \text{ or mol lit}^{-1} \text{ min}^{-1}$$

RATE LAWS

The rate of a reaction is directly proportional to the reactant concentration, each concentration being raised to some power which may be some integer or fraction. Thus, for the reactions given below, rate of reactions are also shown.

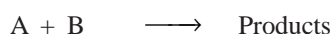


where k is a constant called rate constant for the reaction and m and n are small integers or fractions.

An expression which shows how the reaction rate is related to concentration is called **rate law** or **rate equation**.

ORDER OF A REACTION

The order of a reaction is the sum of powers of concentrations in the rate law. For example, for the reaction



the rate is $k [A]^m [B]^n$ and order of the reaction is $m + n$. Reaction may be classified according to order. Thus, when

- $m + n = 0$ the reaction is zero order reaction
 $m + n = 1$ the reaction is first order reaction
 $m + n = 2$ the reaction is second order reaction

MOLECULARITY OF A REACTION

The number of reactant molecules involved in a reaction is called the molecularity of the reaction. It is always a whole number and can not have zero value. It may be different from the order of reaction.

RATE EQUATIONS FOR DIFFERENT TYPES OF REACTIONS

The rate equations for different types of reactions having different order are summarised in the Table 20.1

TABLE 20.1 : RATE EQUATIONS FOR DIFFERENT TYPES OF REACTIONS.			
Reaction	Reaction Equation	Order of Reaction	Rate constant expression
A \longrightarrow Products	Rate = $k [A]^0$	0	$k = \frac{x}{t}$
B \longrightarrow Products	Rate = $k [A]$	1	$k = \frac{2.303}{t} \log \frac{a}{a-x}$
A + B \longrightarrow Products	Rate = $k [A] [B]$	2	$k = \frac{2.303}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$
2A \longrightarrow Products	Rate = $k [A]^2$	2	$k = \frac{1}{t} \times \frac{x}{a(a-x)}$
3A \longrightarrow Products	Rate = $k [A]^3$	3	$k = \frac{1}{t} \times \frac{x(2a-x)}{2a^2(a-x)^2}$

RATE CONSTANTS AND ITS UNITS

The rate constant is defined as the rate of reaction when the concentration of all reactants is unity. The units of rate constant depend upon the order of the reaction. For various types of reactions the units of rate constant are as follows :

- For a zero order reaction $k = \frac{x}{t} \frac{\text{mol lit}^{-1}}{\text{time}^{-1}}$ or $\text{mol lit}^{-1} \text{time}^{-1}$
 For a 1st order reaction $k = \frac{2.303}{t} \log \frac{a}{a-x} \frac{1}{\text{time}} \times \frac{\text{mol lit}^{-1}}{\text{mol lit}^{-1}} = \text{time}^{-1}$
 For a 2nd order reaction $k = \frac{1 \times x}{t a(a-x)} \frac{1}{\text{time}} \times \frac{\text{mol lit}^{-1}}{\text{mol lit}^{-1} \times \text{mol lit}^{-1}} = \text{mol}^{-1} \text{lit time}^{-1}$
 For a 3rd order reaction $k = \frac{x(2a-x)}{t 2a^2(a-x)^2} \frac{\text{mol lit}^{-1} \times \text{mol lit}^{-1}}{\text{time} \times (\text{mol lit}^{-1})^4} = \text{mol}^{-2} \text{lit}^2 \text{time}^{-1}$

HALF LIFE OF A REACTION

It is defined as the time required for the concentration of a reactant to decrease to half its initial value. It is represented by $t_{1/2}$ or $t_{0.5}$. For a first order reaction $t_{1/2}$ is given by

For a first order reaction $t_{1/2}$ is given by

$$\begin{aligned}
 t_{1/2} &= \frac{2.303}{k} \times \log \frac{a}{a-a/2} \\
 &= \frac{2.303}{k} \times \log \frac{a}{a/2} \\
 &= \frac{2.303}{k} \times \log 2 = \frac{0.693}{k}
 \end{aligned}$$

For a second order reaction $t_{1/2}$ is given by

$$t_{1/2} = \frac{1}{k} \frac{x}{a(a-x)} \text{ where } x = a/2$$

$$= \frac{1}{k} \frac{a/2}{a/2(a - a/2)}$$

$$= \frac{2}{k a} \propto \frac{1}{a}$$

DETERMINATION OF ORDER OF A REACTION

(i) Using Integrated rate equations

This is hit and trial method involving the use of different rate equations. The rate equation which gives the constant value of k corresponds to the correct order of the reaction. In this method different initial concentrations of reactants a , are taken and the concentrations left $(a - x)$ after regular time intervals are measured. These values are substituted in the following equations :

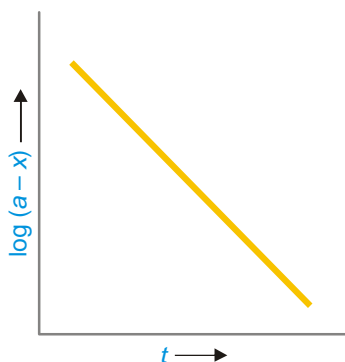
$$\text{for a first order reaction } k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$\text{for a second order reaction } k = \frac{1 \times x}{t \times a(a-x)}$$

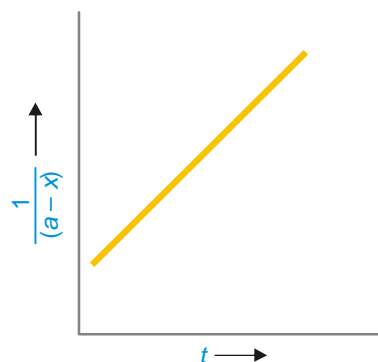
$$\text{and for a third order reaction } k = \frac{a(2a-x)}{t \times 2a^2 \times (a-x)}$$

(ii) Graphical Method

For a reaction $A \longrightarrow \text{Products}$, if the graph between $\log \frac{a}{a-x}$ and t is a straight line, the reaction is of the first order. In case the graph between the $\frac{1}{a-x}$ and t is a straight line the reaction is second order. (Fig. 20.1 and Fig. 20.2)



■ **Figure 20.1**
Plot of $\log \frac{a}{a-x}$ vs t for a 1st order reaction.



■ **Figure 20.2**
Plot of $\log \frac{1}{a-x}$ vs t for a 2nd order reaction.

(iii) Using Half-life Period

Two separate experiments are performed by taking different initial concentrations of a reactant and the time in which the concentration is reduced to half is noted. If the half life is

- | | | |
|-----|--------------------------------------|-----------------------------|
| (a) | independent of initial concentration | order of reaction = 1 |
| (b) | $\propto \frac{1}{[A]}$ | order of reaction = 2 |
| (c) | $\propto \frac{1}{[A]^2}$ | order of reaction = 3 |
| (d) | $\propto \frac{1}{[A]^{n-1}}$ | order of reaction = $n - 1$ |

Also for n th order of reaction

$$n = 1 + \frac{\log [t_1/t_2]}{\log [A_2/A_1]}$$

where A_1 is the initial concentration and t_1 , the half life period in experiment one and A_2 the initial concentration and t_2 , the half life period in second experiment.

(iv) The differential Method

The rate of a reaction of n th order is proportional to n th power of concentration.

$$-\frac{dC}{dt} = kC^n$$

Two experiments with different initial concentrations are performed and the value of n , the order of reaction, is determined by using the formula

$$n = \frac{\log \left(-\frac{dC_1}{dt} \right) - \log \left(-\frac{dC_2}{dt} \right)}{\log C_1 - \log C_2}$$

EFFECT OF TEMPERATURE ON REACTION RATE

Temperature coefficient is given by

$$\text{Temperature Coefficient} = \frac{k_{35^\circ}}{k_{25^\circ}} = \frac{k_{308}}{k_{298}} = 2 \text{ to } 3$$

Thus an increase of temperature by 10°C increases the rate of reaction by 2 to 3 times.

ARRHENIUS EQUATION

The relation between the rate constant, k , for a reaction and the temperature is given by

$$k = A e^{-E_a/RT}$$

where E_a is the activation energy, R the gas constant and T , the absolute temperature.

Taking logarithms we have

$$\log k = -\frac{E_a}{RT} + \log A$$

If k_1 and k_2 are the values of rate constant at temperatures T_1 and T_2 we have

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

ADDITIONAL SOLVED PROBLEMS

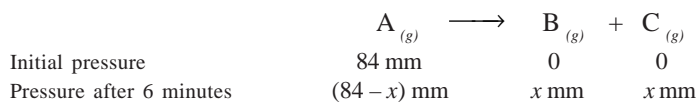
SOLVED PROBLEM 1. In the first order reaction



the initial pressure of A is 84 mm and the total pressure at the end of 6 minutes is 110 mm. Calculate the half life of the reaction.

SOLUTION :

The reaction is



$$\text{After 6 minutes the total pressure} = 84 - x + x + x \text{ mm} = 84 + x$$

$$= 110 \text{ mm}$$

$$\text{or} \quad 84 + x = 110 \text{ mm}$$

$$\text{or} \quad x = 26 \text{ mm}$$

(i) To calculate the value of rate constant

Formula used

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

Quantities given

$$t = 6 \text{ minutes}$$

Substitution of values

$$a = 84 \text{ mm} \quad a - x = 84 - 26 \text{ mm} = 58 \text{ mm}$$

$$\begin{aligned} k &= \frac{2.303}{6 \text{ min}} \log \frac{84 \text{ mm}}{58 \text{ mm}} \\ &= \frac{2.303}{6 \text{ min}} \log 1.4482 \\ &= 0.3838 \times 0.1608 \text{ min}^{-1} \\ &= 0.0617 \text{ min}^{-1} \end{aligned}$$

(ii) To calculate half life period**Formula used**

$$t_{1/2} = \frac{0.693}{k}$$

Substitution of values

$$t_{1/2} = \frac{0.693}{0.0617 \text{ min}^{-1}} = \mathbf{11.23 \text{ min}}$$

SOLVED PROBLEM 2. The rate constant for a reaction at 20 °C is half of the rate constant at 30 °C. Calculate the energy of activation of the reaction. [$R = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$]

SOLUTION :**Formula used**

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Quantities given

$$\frac{k_2}{k_1} = 2$$

$$R = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$T_1 = 20 + 273 = 293 \text{ K}$$

$$T_2 = 273 + 30 = 303 \text{ K}$$

Substitution of values

$$\log 2 = \frac{E_a}{2.303 \times 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}} \left[\frac{303 \text{ K} - 293 \text{ K}}{303 \text{ K} \times 293 \text{ K}} \right]$$

or

$$\begin{aligned} E_a &= \frac{2.303 \times 1.987 \times 0.3010 \times 303 \times 293}{10} \\ &= 12228.36 \text{ cal} \\ &= \mathbf{12.22836 \text{ kcal}} \end{aligned}$$

SOLVED PROBLEM 3. In a first order reaction, half of the reactant is decomposed in 1000 sec. How long will it be until 1/3 of the reactant is left ?

SOLUTION :**(i) To calculate the value of rate constant****Formula used**

$$k = \frac{0.693}{t_{1/2}}$$

Quantities given

$$t_{1/2} = 1000 \text{ sec}$$

Substitution of values

$$k = \frac{0.693}{1000 \text{ sec}} = 0.000693 \text{ sec}^{-1}$$

(ii) To calculate time when 1/3 of the reactant is left**Formula used**

$$t = \frac{2.303}{k} \log \frac{a}{a-x}$$

Quantities given

$$a = 1 \quad x = 2/3$$

$$a - x = 1/3$$

$$k = 0.000693 \text{ sec}^{-1}$$

Substitution of values

$$\begin{aligned} t &= \frac{2.303}{0.000693 \text{ sec}^{-1}} \log \frac{1}{1/3} \\ &= 3323.23 \times \log 3 \text{ sec} \\ &= 3323.23 \times 0.4771 \text{ sec} \\ &= \mathbf{1585.51 \text{ sec}} \end{aligned}$$

SOLVED PROBLEM 4. A first order reaction is 15% complete in 20 minutes. How long will it take to be 60% complete?

SOLUTION :**(i) To calculate the value of rate constant****Formula used**

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

Quantities given

$$a = 100$$

$$x = 15$$

$$a - x = 85$$

$$t = 20 \text{ minutes}$$

Substitution of values

$$\begin{aligned} k &= \frac{2.303}{20 \text{ min}} \log \frac{100}{85} \\ &= 0.11515 \times \log 1.17647 \text{ min}^{-1} \\ &= 0.11515 \times 0.07058 \text{ min}^{-1} \\ &= 8.127 \times 10^{-3} \text{ min}^{-1} \end{aligned}$$

(ii) To calculate the time when reaction is 60% complete.**Formula used**

$$t = \frac{2.303}{k} \log \frac{a}{a-x}$$

Quantities given

$$k = 8.127 \times 10^{-3} \text{ min}^{-1}$$

$$a = 100$$

$$a - x = 40$$

Substitution of values

$$\begin{aligned} t &= \frac{2.303}{8.127 \times 10^{-3} \text{ min}^{-1}} \log \frac{100}{40} \\ &= 283.376 \times \log 2.5 \text{ min} \\ &= 283.376 \times 0.3979 \text{ min} \\ &= \mathbf{112.76 \text{ min}} \end{aligned}$$

SOLVED PROBLEM 5. 50% of H_2O_2 decomposes in 10 minutes in an experiment. Find out its velocity coefficient if the reaction is first order.

SOLUTION :**Formula used**

$$k = \frac{0.693}{t_{1/2}}$$

Quantities given

$$t_{1/2} = 10 \text{ min}$$

Substitution of value

$$k = \frac{0.693}{10 \text{ min}} = \mathbf{0.0693 \text{ min}^{-1}}$$

SOLVED PROBLEM 6. If a first order reaction is half completed in 100 seconds, calculate the time required for 99% of the reaction to be completed.

SOLUTION : (i) To calculate the value of rate constant**Formula used**

$$k = \frac{0.693}{t_{1/2}}$$

Quantities given

$$t_{1/2} = 100 \text{ sec}$$

Substitution of values

$$k = \frac{0.693}{100 \text{ sec}} = 0.00693 \text{ sec}^{-1}$$

(ii) To calculate the time for 99% of the reaction to be completed**Formula used**

$$t = \frac{2.303}{k} \log \frac{a}{a-x}$$

Quantities given

$$k = 0.00693 \text{ sec}^{-1}$$

$$a = 100$$

$$x = 99$$

$$a - x = 1$$

Substitution of values

$$\begin{aligned} t &= \frac{2.303}{0.00693 \text{ sec}^{-1}} \log \frac{100}{1} \\ &= 332.32 \times \log 100 \text{ sec} \\ &= 332.32 \times 2 \text{ sec} = \mathbf{664.64 \text{ sec}} \end{aligned}$$

SOLVED PROBLEM 7. 50% of a first order reaction is completed in 23 minutes. Calculate the time required to complete 90% of the reaction.

SOLUTION : (i) To calculate the value of rate constant**Formula used**

$$k = \frac{0.693}{t_{1/2}}$$

Quantity given

$$t_{1/2} = 23 \text{ minutes}$$

Substitution of values

$$k = \frac{0.693}{23 \text{ min}} = 0.03013 \text{ min}^{-1}$$

(ii) To calculate the time required to complete 90% of reaction**Formula used**

$$t = \frac{2.303}{k} \log \frac{a}{a-x}$$

Quantities given

$$k = 0.03013 \text{ min}^{-1}$$

$$a = 100$$

$$x = 90$$

$$a - x = 10$$

Substitution of values

$$\begin{aligned} t &= \frac{2.303}{0.03013 \text{ min}^{-1}} \log \frac{100}{10} \\ &= 76.44 \text{ min} \times \log 10 \\ &= \mathbf{76.44 \text{ min}} \quad [\because \log 10 = 1] \end{aligned}$$

SOLVED PROBLEM 8. From the following show that the decomposition of hydrogen peroxide in aqueous solution is a first order reaction.

Time (min)	0	15	30
V	25.4	9.83	3.81

where V is the volume of KMnO_4 required in ml to decompose a definite volume of hydrogen peroxide.

SOLUTION :**Formula used**

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

Quantities given

$$\begin{array}{lll}
 t = 15 \text{ min} & a = 25.4 & a - x = 9.83 \\
 \text{and } t = 30 \text{ min} & a = 25.4 & a - x = 3.81
 \end{array}$$

Substitution of values

$$\begin{aligned}
 k &= \frac{2.303}{15 \text{ min}} \log \frac{25.4}{9.83} & k &= \frac{2.303}{30 \text{ min}} \log \frac{25.4}{3.81} \\
 &= 0.1535 \text{ min}^{-1} \times \log 2.5839 & k &= 0.07676 \text{ min}^{-1} \times \log 6.6666 \\
 &= 0.1535 \text{ min}^{-1} \times 0.41227 & &= 0.07676 \text{ min}^{-1} \times 0.8239 \\
 &= 0.06328 & &= 0.06324
 \end{aligned}$$

Since the value of k is constant, the reaction is of first order.

SOLVED PROBLEM 9. 75% of a reaction of the first order was completed in 32 minutes. When was it half completed ?

SOLUTION :**(i) To calculate the value of rate constant****Formula used**

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

Quantities given

$$t = 32 \text{ min}$$

$$a = 100$$

$$x = 75$$

$$a - x = 25$$

Substitution of values

$$\begin{aligned}
 k &= \frac{2.303}{32 \text{ min}} \log \frac{100}{25} \\
 &= 0.0171969 \times \log 4 \\
 &= 0.71967 \times 0.6021 \\
 &= \mathbf{0.0433 \text{ min}^{-1}}
 \end{aligned}$$

(ii) To calculate half life period**Formula used**

$$t_{1/2} = \frac{0.693}{k}$$

Substitution of values

$$t_{1/2} = \frac{0.693}{0.0433 \text{ min}^{-1}} = \mathbf{16.0 \text{ min}}$$

SOLVED PROBLEM 10. In a gaseous reaction, the time for half change ($t_{1/2}$) for various partial pressures (P) was as follows :

$P(\text{mm})$	500	600	800	1000
$t_{1/2}(\text{min})$	268	223	168	134

Calculate the order of the reaction.

SOLUTION :

Since the value of $t_{1/2}$ is varying with the initial pressure, the reaction can not be of first order.

Formula given

$$k = \frac{1}{t_{1/2}(a)} \text{ for a second order reaction}$$

Quantities given

$$t_{1/2} = 268$$

$$223$$

$$168$$

$$134 \text{ minutes}$$

$$a = 500$$

$$600$$

$$800$$

$$1000 \text{ mm}$$

Substitution of values

$$\begin{aligned}
 k &= \frac{1}{268 \times 500} = 7.462 \times 10^{-6} \\
 k &= \frac{1}{223 \times 600} = 7.473 \times 10^{-6}
 \end{aligned}$$

$$k = \frac{1}{168 \times 800} = 7.440 \times 10^{-6}$$

$$k = \frac{1}{134 \times 1000} = 7.460 \times 10^{-6}$$

Since the value of k is constant, the reaction is of second order.

SOLVED PROBLEM 11. For a certain reaction the rate constant $k = 2.46 \times 10^{-5}$ at 273 K and 1.63×10^{-3} at 303 K. Calculate the energy of activation for the reaction.

SOLUTION :

Formula used

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Quantities given

$$k_1 = 2.46 \times 10^{-5}$$

$$T_1 = 273 \text{ K}$$

$$R = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$k_2 = 1.63 \times 10^{-3}$$

$$T_2 = 303 \text{ K}$$

Substitution of values

$$\log \frac{1.63 \times 10^{-3}}{2.46 \times 10^{-5}} = \frac{E_a}{2.303 \times 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}} \times \left[\frac{303 \text{ K} - 273 \text{ K}}{303 \text{ K} \times 273 \text{ K}} \right]$$

$$E_a = \frac{1.8212 \times 2.303 \times 1.987 \times 303 \times 273}{30}$$

$$= \mathbf{22979 \text{ cal}}$$

SOLVED PROBLEM 12. The half life for a first order reaction is 2.5×10^3 sec. How long will it take for 1/5th of the reactant to be left behind ?

SOLUTION :

(i) To calculate the value of rate constant

Formula used

$$k = \frac{0.693}{t_{1/2}}$$

Quantities given

$$t_{1/2} = 2.5 \times 10^3 \text{ sec.}$$

Substitution of value

$$k = \frac{0.693}{2.5 \times 10^3 \text{ sec.}} = 2.772 \times 10^{-4} \text{ sec}^{-1}$$

(ii) To calculate the time for 1/5th of the reaction to be left behind

Formula used

$$t = \frac{2.303}{k} \log \frac{a}{a-x}$$

Quantities given

$$a = 100$$

$$a-x = \frac{1}{5} \times 100 = 20$$

$$k = 2.772 \times 10^{-4} \text{ sec}^{-1}$$

Substitution of values

$$t = \frac{2.303}{2.772 \times 10^{-4} \text{ sec}^{-1}} \times \log \frac{100}{20}$$

$$= 8308.08 \times \log 5 \text{ sec}$$

$$= 8308.08 \times 0.6990 \text{ sec}$$

$$= \mathbf{5807.34 \text{ sec}}$$

SOLVED PROBLEM 13. It was found that a solution of cane sugar in water hydrolysed to a extent of 25% in one hour. Calculate the time that would be taken for the sugar to be 50% hydrolysed assuming the reaction is of the first order.

SOLUTION : (i) To calculate the value of rate constant**Formula used**

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

Quantities given

$$a = 100$$

$$x = 25$$

$$a - x = 75$$

$$t = 60 \text{ min}$$

Substitution of values

$$\begin{aligned} k &= \frac{2.303}{60 \text{ min}} \log \frac{100}{75} \\ &= 0.03838 \text{ min}^{-1} \times \log 4/3 \\ &= 0.038383 \text{ min}^{-1} \times \log 1.3333 \\ &= 4.794 \times 10^{-3} \text{ min}^{-1} \end{aligned}$$

(ii) To calculate the half time period**Formula used**

$$t_{1/2} = \frac{0.693}{k}$$

Substitution of value

$$\begin{aligned} t_{1/2} &= \frac{0.693}{4.794 \times 10^{-3} \text{ min}^{-1}} \\ &= \mathbf{144.5 \text{ min}} \end{aligned}$$

SOLVED PROBLEM 14. Calculate the activation energy of a reaction whose rate constant gets double for 10 °C rise in temperature.

SOLUTION :**Formula used**

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Quantities given

$$\frac{k_2}{k_1} = 2$$

$$R = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$T_1 = 27 + 273 = 300 \text{ K}$$

$$T_2 = 372 + 273 = 310 \text{ K}$$

Substitution of values

$$\log 2 = \frac{E_a}{2.303 \times 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}} \left[\frac{310 - 300}{300 \times 310} \right]$$

or

$$E_a = \frac{0.3010 \times 2.303 \times 1.987 \times 300 \times 310}{10}$$

$$= \mathbf{12809.77 \text{ cal}}$$

SOLVED PROBLEM 15. For a certain reaction the values of the rate constants at 25 °C and 65 °C were found to be 3.46×10^{-5} and 4.86×10^{-3} respectively. Calculate the energy of activation for the reaction.

SOLUTION :**Formula used**

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Quantities given

$$k_2 = 4.86 \times 10^{-3}$$

$$k_1 = 3.46 \times 10^{-5}$$

$$T_1 = 25 + 273 = 298 \text{ K}$$

$$T_2 = 65 + 273 = 338 \text{ K}$$

$$R = 1.987 \text{ cal}^{-1} \text{ K}^{-1} \text{ mol}^{-1}$$

Substitution of values

$$\log \frac{4.86 \times 10^{-3}}{3.46 \times 10^{-5}} = \frac{E_a}{2.303 \times 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}} \left[\frac{338 \text{ K} - 298 \text{ K}}{338 \text{ K} \times 298 \text{ K}} \right]$$

or

$$E_a = \frac{2.14845 \times 2.303 \times 1.987 \times 338 \times 298}{40}$$

$$= 24757.12 \text{ cal}$$

SOLVED PROBLEM 16. Calculate the half life period for the first order reaction whose rate constant is $1.052 \times 10^{-3} \text{ sec}^{-1}$.

SOLUTION :**Formula used**

$$t_{1/2} = \frac{0.693}{k}$$

Quantities given

$$k = 1.052 \times 10^{-3} \text{ sec}^{-1}$$

Substitution of values

$$t = \frac{0.693}{1.052 \times 10^{-3} \text{ sec}^{-1}} = 659 \text{ sec}$$

SOLVED PROBLEM 17. The rate constant for the first order reaction at 45°C is twice that at 35°C . Find the energy of activation of the reaction.

SOLUTION :**Formula used**

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Quantities given

$$\frac{k_2}{k_1} = 2$$

$$R = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$T_1 = 45 + 273 = 318 \text{ K}$$

$$T_2 = 35 + 273 = 308 \text{ K}$$

Substitution of values

$$\log 2 = \frac{E_a}{2.303 \times 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}} \left[\frac{318 \text{ K} - 308 \text{ K}}{318 \text{ K} \times 308 \text{ K}} \right]$$

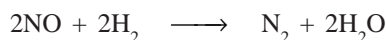
or

$$E_a = \frac{0.3010 \times 2.303 \times 1.987 \times 318 \times 308}{10}$$

$$= 13490.75 \text{ cal}$$

$$= 13.49075 \text{ kcal}$$

SOLVED PROBLEM 18. In the reaction



equimolar mixture of gas at 336 mm Hg initial pressure was changed in 108 seconds. When the initial pressure was 288 mm it was half changed in 148 seconds. Determine the order of the reaction.

SOLUTION :**Formula used**

$$\frac{t_2}{t_1} = \left[\frac{A_1}{A_2} \right]^{n-1}$$

Quantities given

$$t_2 = 108 \text{ sec}$$

$$A_1 = 288 \text{ mm}$$

$$t_1 = 148 \text{ sec}$$

$$A_2 = 336 \text{ mm}$$

Substitution of values

$$\frac{108 \text{ sec}}{148 \text{ sec}} = \left(\frac{288 \text{ mm}}{336 \text{ mm}} \right)^{n-1}$$

Taking logarithms

$$\log \frac{108}{148} = n - 1 \times \log \frac{288}{336}$$

$$\text{or} \quad n - 1 = \frac{\log(108/148)}{\log(288/336)}$$

$$\begin{aligned} \text{or} \quad n &= 1 + \left(\frac{-0.1368}{-0.0669} \right) \\ &= 1 + 2 \\ &= 3 \end{aligned}$$

SOLVED PROBLEM 19. If a unimolecular reaction is one quarter completed in 100 minutes, what is the specific rate constant k ? ($k = \frac{2.303}{t} \log \frac{a}{a-x}$)

SOLUTION :

Formula used

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

Quantities given

$$a = 100$$

$$x = 25$$

$$a - x = 75$$

$$t = 100 \text{ minutes}$$

Substitution of values

$$\begin{aligned} k &= \frac{2.303}{100 \text{ min}} \log \frac{100}{75} \\ &= \frac{2.303}{100} \text{ min}^{-1} \times \log 1.333 \\ &= 0.02303 \text{ min}^{-1} \times 0.1249 \\ &= 2.8764 \times 10^{-3} \text{ min}^{-1} \end{aligned}$$

SOLVED PROBLEM 20. Saponification of ethyl acetate was carried out by NaOH using equal concentration of the two at 310 K. At regular intervals 20 ml samples of reaction mixture were titrated against the standard acid and the following results were obtained :

Time (min)	0	4.89	10.07	22.63
Vol. of acid used (ml)	47.65	38.92	32.62	22.58

Show that the reaction is of second order.

SOLUTION :

Formula used

$$k = \frac{1}{t} \times \frac{x}{a(a-x)}$$

Quantities given

$$t = 4.89 \text{ min}$$

$$10.07$$

$$22.63 \text{ min}$$

$$a = 47.65$$

$$x = 8.73$$

$$15.030$$

$$25.070$$

$$a - x = 38.92$$

$$32.62$$

$$22.58$$

Substitution of values

$$k = \frac{1 \times 8.73}{4.89 \text{ min} \times 47.65 \times 38.92} = 0.000960 \text{ min}^{-1}$$

$$k = \frac{1 \times 15.030}{10.07 \text{ min} \times 47.65 \times 32.62} = 0.000960 \text{ min}^{-1}$$

and

$$k = \frac{1}{22.63 \text{ min}} \times \frac{25.070}{47.65 \times 22.58} = 0.000986 \text{ min}^{-1}$$

Since the value of k is constant, the reaction is of first order.

SOLVED PROBLEM 21. If the initial concentration of both the reactants following a second order reaction kinetics are the same, then how long will it take for the 70% completion of the reaction, if 30% of the reaction is completed in 12 minutes.

SOLUTION : (i) To calculate the value of rate constant

Formula used

$$k = \frac{1}{t} \times \frac{x}{a(a-x)}$$

Quantities given

$$t = 12 \text{ min}$$

$$x = 30$$

$$a = 100$$

Substitution of values

$$\begin{aligned} k &= \frac{1}{12 \text{ min}} \times \frac{30}{100 \times 70} \\ &= 3.5714 \times 10^{-4} \end{aligned}$$

(ii) To calculate the time for 70% completion of reaction

Formula used

$$t = \frac{1}{k} \times \frac{x}{a(a-x)}$$

Quantities given

$$x = 70$$

$$a = 100$$

$$k = 3.5714 \times 10^{-4} \text{ min}^{-1}$$

Substitution of values

$$\begin{aligned} t &= \frac{1}{3.5714 \times 10^{-4} \text{ min}^{-1}} \times \frac{70}{100 \times 30} \\ &= \mathbf{62.199 \text{ min}} \end{aligned}$$

SOLVED PROBLEM 22. The specific reaction rate for the decomposition of N_2O_5 vapour is found to be 3.46×10^{-5} at 298 K and 4.87×10^{-3} at 338 K. Determine the activation energy of the reaction.

SOLUTION :

Formula given

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$$

Quantities given

$$k_2 = 4.87 \times 10^{-3}$$

$$T_2 = 338 \text{ K}$$

$$R = 8.314 \text{ J K}^{-1}$$

$$k_1 = 3.46 \times 10^{-5}$$

$$T_1 = 298 \text{ K}$$

Substituting of values

$$\log \frac{4.87 \times 10^{-3}}{3.46 \times 10^{-5}} = \frac{E_a}{2.303 \times 8.314 \text{ J}} \left[\frac{338 \text{ K} - 298 \text{ K}}{338 \text{ K} \times 298 \text{ K}} \right]$$

or

$$2.1484 = \frac{E_a}{2.303 \times 8.314 \text{ J}} \left[\frac{40 \text{ K}}{338 \text{ K} \times 298 \text{ K}} \right]$$

or

$$\begin{aligned} E_a &= \frac{2.1484 \times 2.303 \times 8.314 \text{ J} \times 338 \times 298}{40} \\ &= 103583.86 \text{ J} \\ &= \mathbf{103.58386 \text{ kJ}} \end{aligned}$$

SOLVED PROBLEM 23. Compound A decomposes to form B and C and reaction is first order. At 25 °C the rate constant for the reaction is 0.45 sec^{-1} . What is the half life of A at 25 °C ?

SOLUTION :**Formula used**

$$t_{1/2} = \frac{0.693}{k}$$

Quantity given

$$k = 0.45 \text{ sec}^{-1}$$

Substitution of value

$$\begin{aligned} t_{1/2} &= \frac{0.693}{0.45 \text{ sec}^{-1}} \\ &= \mathbf{1.54 \text{ sec}} \end{aligned}$$

SOLVED PROBLEM 24. For the first order reaction the half life period is 30 minutes. What is the time taken for 75% of the completion of the reaction ?

SOLUTION : (i) To calculate the value of rate constant**Formula used**

$$k = \frac{0.693}{t_{1/2}}$$

Quantity given

$$t_{1/2} = 30 \text{ min}$$

Substitution of value

$$k = \frac{0.693}{30 \text{ min}} = 0.0231 \text{ min}^{-1}$$

(ii) To calculate the time for 75% of completion of reaction**Formula used**

$$k = \frac{2.303}{0.231 \text{ min}} \log \frac{a}{a-x}$$

Quantities given

$$k = 0.0231 \text{ min}^{-1}$$

$$a = 100$$

$$x = 75$$

Substitution of values

$$\begin{aligned} t &= \frac{2.303}{0.231 \text{ min}^{-1}} \log \frac{100}{100-75} \\ &= \frac{2.303}{0.231} \text{ min} \times \log 4 \\ &= \frac{2.303}{0.231} \text{ min} \times 0.6021 \\ &= \mathbf{60 \text{ min}} \end{aligned}$$

SOLVED PROBLEM 25. Calculate the activation energy of a reaction whose rate constant doubles when the temperature is raised from 22 °C to 32 °C.

SOLUTION :**Formula used**

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$$

Quantities given

$$\frac{k_2}{k_1} = 2$$

$$R = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$$

$$T_2 = 32 + 273 = 305 \text{ K}$$

$$T_1 = 22 + 273 = 295 \text{ K}$$

Substitution of values

$$\begin{aligned}\log 2 &= \frac{E_a}{2.303 \times 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}} \times \left[\frac{305 \text{ K} - 295 \text{ K}}{305 \text{ K} \times 295 \text{ K}} \right] \\ &= \frac{0.3010 \times 2.303 \times 1.987 \times 305 \times 295}{10} \text{ cal} \\ \text{or} \quad &= 123931.1 \text{ cal} \\ &= \mathbf{12.3931 \text{ kcal}}\end{aligned}$$

SOLVED PROBLEM 26. The specific reaction rate of a chemical reaction at 273 K and 303 K are $2.45 \times 10^{-5} \text{ sec}^{-1}$ and $16.2 \times 10^{-4} \text{ sec}^{-1}$ respectively. Calculate the energy of activation ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

SOLUTION :**Formula used**

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R} \left[\frac{T_2 - T_1}{T_2 \times T_1} \right]$$

Quantities given

$$k_2 = 16.2 \times 10^{-4} \text{ sec}^{-1}$$

$$T_2 = 303 \text{ K}$$

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$k_1 = 2.45 \times 10^{-5} \text{ sec}^{-1}$$

$$T_1 = 273 \text{ K}$$

Substitution of values

$$\log \frac{16.2 \times 10^{-4} \text{ sec}^{-1}}{2.45 \times 10^{-5} \text{ sec}^{-1}} = \frac{E_a}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1}} \left[\frac{303 \text{ K} - 273 \text{ K}}{303 \text{ K} \times 273 \text{ K}} \right]$$

or

$$\begin{aligned}E_a &= \frac{1.8203 \times 2.303 \times 8.314 \times 303 \times 273}{30} \\ &= 96101.67 \text{ J} \\ &= \mathbf{96.10167 \text{ kJ}}\end{aligned}$$

SOLVED PROBLEM 27. In the Arrhenius equation for a certain reaction, the value of A and E_a (activation energy) are $4 \times 10^{13} \text{ sec}^{-1}$ and 98.6 kJ mol^{-1} respectively. If the reaction is of first order, at what temperature will its half life period be 10 minutes ?

SOLUTION : (i) To calculate the value of rate constant**Formula used**

$$k = \frac{0.693}{t_{1/2}}$$

Quantities given

$$t_{1/2} = 10 \text{ min}$$

Substitution of values

$$k = \frac{0.693}{10 \times 60 \text{ sec}} = 1.155 \times 10^{-3} \text{ sec}^{-1}$$

(ii) To calculate the temperature**Formula used**

$$k = Ae^{-E_a/RT}$$

or

$$\log k = \frac{E_a}{2.303 RT} + \log A$$

Quantities given

$$k_2 = 1.55 \times 10^{-3} \text{ sec}^{-1}$$

$$A = 4 \times 10^{13} \text{ sec}^{-1}$$

$$E_a = 98.6 \text{ kJ mol}^{-1}$$

$$R = 8.314 \times 10^{-3} \text{ kJ mol}^{-1}$$

Substitution of values

$$\begin{aligned} \log 1.55 \times 10^{-3} &= \log (4 \times 10^{13}) - \frac{98.6 \text{ kJ}}{2.303 \times 8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1} \times T} \\ -2.9374 &= 13.6021 - \frac{5.1496 \times 10^3}{T} \\ T &= \frac{5.1496 \times 10^3}{13.6021 + 2.9374} \\ &= \mathbf{311.35 \text{ K}} \end{aligned}$$

SOLVED PROBLEM 28. The catalyst decomposition of N_2O by gold at 900°C and at initial pressure of 200 mm is 50% complete in 53 minutes and 73% complete in 100 minutes.

(a) What is the order of the reaction ?

(b) How much of it will decompose in 100 minutes at initial pressure of 600 mm ?

SOLUTION : (i) To calculate the order of reaction**Formula used**

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \text{ for 1st order reaction}$$

Quantities given

$$a = 100$$

$$x = 50 \text{ and } 73$$

$$t = 53 \text{ mts and } 100 \text{ mts}$$

$$a-x = 100 - 50 \text{ and } 100 - 73 = 27$$

Substitution of values

$$k = \frac{2.303}{53} \log \frac{100}{50}$$

and

$$k = \frac{2.303}{100} \log \frac{100}{27}$$

$$k = 0.013864 \text{ min}^{-1}$$

$$k = 0.013095 \text{ min}^{-1}$$

Since k is constant the reaction is of **first** order

(ii) To calculate the amount decomposed in 100 minutes at initial pressure of 600 mm**Formula used**

$$\% \text{ decomposition} = \frac{\text{Initial pressure} \times \% \text{ decomposed}}{100}$$

[\because It is independent of initial conc. for 1st order reaction]

Quantities given

$$\text{Initial pressure} = 600$$

$$\% \text{ decomposed} = 73$$

Substitution of values

$$\begin{aligned} \text{Amount of } \text{N}_2\text{O} \text{ decomposed} &= \frac{600 \text{ mm} \times 73}{100} \\ &= \mathbf{438 \text{ mm}} \end{aligned}$$

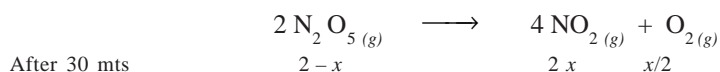
SOLVED PROBLEM 29 The decomposition of N_2O_5 according to the equation :



is a first order reaction. After 30 minutes from the start of decomposition in a closed vessel, the total pressure developed is found to be 284.5 mm of Hg and on complete decomposition, the total pressure is 584.5 mm of Hg. Calculate the rate constant of the reaction.

SOLUTION :

The reaction is



$$\begin{aligned} \text{The initial pressure of N}_2\text{O}_5 &= \frac{\text{No. of moles of N}_2\text{O}_5}{\text{Total no. of moles}} \\ &= \frac{2.303}{50} \times 58.4 \text{ mm} = 233.8 \text{ mm} \end{aligned}$$

Let the amt. of N_2O_5 decomposed after 30 mt. be $= x$

then pressure due to $\text{N}_2\text{O}_5 = 233.8 - x \text{ mm}$

pressure due to $\text{NO}_2 = 2x$

and pressure due to $\text{O}_2 = x/2$

Total pressure after 30 minutes $= 233.8 - x + 2x + x/2 = 284.5 \text{ mm}$ (given)

$$233.8 + 3x/2 = 284.5 \text{ mm}$$

$$\text{or } x = \frac{(284.5 - 233.8) \times 2}{3} = 33.8 \text{ mm}$$

Formula used

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

Quantities given

$$t = 30 \text{ minutes} \quad a = 233.8 \text{ mm} \quad x = 33.8 \text{ mm} \quad a - x = 233.8 - 200 \text{ mm} = 33.8 \text{ mm}$$

Substitution of values

$$\begin{aligned} k &= \frac{2.303}{30} \log \frac{233.8 \text{ mm}}{200 \text{ mm}} \\ &= 0.7676 \text{ min}^{-1} \times \log 1.169 \\ &= 0.07676 \text{ min}^{-1} \times 0.0678 \\ &= 0.005204 \text{ min}^{-1} \\ &= \mathbf{5.204 \times 10^{-3} \text{ min}^{-1}} \end{aligned}$$

SOLVED PROBLEM 30. What will be initial rate of reaction, if its rate constant is 10^{-3} min^{-1} and the concentration of the reactant is 0.2 mol dm^{-3} ? How much of the reactant will be converted into the products after 200 minutes?

Solution : (i) To calculate the initial rate

Formula used

$$\text{Rate of reaction} = k[A]$$

Quantities given

$$k = 10^{-3} \text{ min}^{-1}$$

$$[A] = 0.2 \text{ mol dm}^{-3}$$

Substitution of values

$$\text{Rate of reaction} = 10^{-3} \text{ min}^{-1} \times 0.2 \text{ mol dm}^{-3} = \mathbf{2 \times 10^{-4} \text{ dm}^{-3} \text{ min}^{-1}}$$

(ii) To calculate the % decomposition after 200 minutes

Formula used

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

or

$$\log \frac{a}{a-x} = \frac{k t}{2.303}$$

Quantities given

$$k = 10^{-3} \text{ min}^{-1}$$

$$t = 200 \text{ min}$$

Substitution of values

$$\log \frac{a}{a-x} = \frac{10^{-3} \text{ min}^{-1} \times 200 \text{ min}}{2.303}$$

$$= 8.684 \times 10^{-2}$$

or

$$\frac{a}{a-x} = \text{Antilog } (8.684 \times 10^{-2})$$

$$\frac{a}{a-x} = 1.22$$

or

$$a = 1.22 a - 1.22 x$$

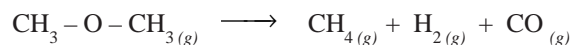
$$122 x = 0.22 a$$

or

$$x = \frac{0.22 a}{1.22}$$

$$\% \text{ Decomposition} = \frac{2303}{t} \times 100 = 18\%$$

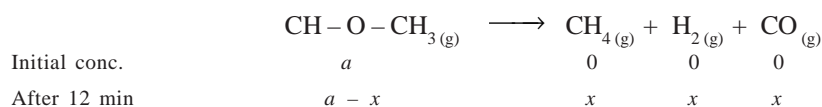
SOLVED PROBLEM 31. The gas phase decomposition of dimethylether follows first order kinetics :



The reaction is carried out in a constant volume container at 500 °C and has a half life of 14.5 minutes. Initially only dimethyl ether is present at a pressure of 0.40 atm. What is the total pressure of the system after 12 minutes assuming ideal gas behavior ?

SOLUTION : (i) To calculate the initial concentration of $\text{CH}_3-\text{O}-\text{CH}_3$

The reaction is



$$\text{Total Initial Conc., } a, \text{ of } \text{CH}_3\text{OCH}_3 = \frac{n}{V}$$

Formula used

$$PV = nRT$$

or

$$\frac{n}{V} = \frac{P}{RT}$$

Quantities given

$$P = 0.4 \text{ atm}$$

$$R = 0.082 \text{ atm lit K}^{-1} \text{ mol}^{-1}$$

$$T = 500 + 273 = 773 \text{ K}$$

Substitution of values

$$a = \frac{n}{V} = \frac{0.4 \text{ atm}}{0.082 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 773 \text{ K}}$$

$$= 6.31 \times 10^{-3} \text{ mol lit}^{-1}$$

(ii) To calculate of $\text{CH}_3-\text{O}-\text{CH}_3$ decomposed after 12 minutes

Formula used

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

Quantities given

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{14.5 \text{ min}} = 4.779 \times 10^{-2} \quad t = 12 \text{ min} \quad a = 6.31 \times 10^{-3} \text{ mol lit}^{-1}$$

Substitution of values

$$4.779 \times 10^{-2} \text{ min}^{-1} = \frac{2.303}{t} \times \log \frac{a}{a-x}$$

or $\log \frac{a}{a-x} = \frac{4.779 \times 10^{-2} \times 12}{2.303} = 0.2490$

or $\frac{a}{a-x} = \text{antilog}(0.2490) = 1.7742$

or $a-x = \frac{a}{1.7742} = \frac{6.31 \times 10^{-3}}{1.7742} \text{ mol lit}^{-1} \quad [\because a = 6.31 \times 10^{-3} \text{ mol lit}^{-1}]$

$$= 3.556 \times 10^{-3} \text{ mol lit}^{-1}$$

or $x = 6.31 \times 10^{-3} - 3.556 \times 10^{-3} \text{ mol lit}^{-1}$

$$= 2.754 \times 10^{-3} \text{ mol lit}^{-1}$$

Total no. of moles after 12 minutes $= a - x + x + x + x$

$$= a + 2x$$

$$= 6.31 \times 10^{-3} + 2 \times 2.754 \times 10^{-3} \text{ mol lit}^{-1}$$

$$= 11.818 \times 10^{-3} \text{ mol lit}^{-1}$$

(iii) To calculate total pressure of the system after 12 minutes**Formula used**

$$P = \frac{n}{V} R T$$

Quantities given

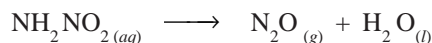
$$\frac{n}{V} = 11.818 \times 10^{-3} \text{ mol lit}^{-1} \quad R = 0.082 \text{ atm lit K}^{-1} \text{ mol}^{-1} \quad T = 773 \text{ K}$$

Substitution of values

$$P = 11.818 \times 10^{-3} \text{ mol lit}^{-1} \times 0.082 \text{ atm lit K}^{-1} \text{ mol}^{-1} \times 773 \text{ K}$$

$$= \mathbf{0.709 \text{ atm}}$$

SOLVED PROBLEM 32. The half life period of first order decomposition of nitramide is 2.1 hour at 15 °C



If 6.2 g of NH_2NO_2 is allowed to decompose, calculate

- (a) time for NH_2NO_2 to decompose 99%; and
 (b) volume of dry N_2O produced at this point measured at STP.

SOLUTION : (i) To calculate time for 99% decomposition**Formula used**

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \quad \text{or} \quad t = \frac{2.303}{k} \log \frac{a}{a-x}$$

Quantities given

$$a = 100 \quad x = 99 \quad a - x = 1 \quad k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.1 \text{ hr}} = 0.33 \text{ hr}^{-1}$$

Substitution of values

$$\begin{aligned} t &= \frac{2.303}{0.33 \text{ hr}^{-1}} \log \frac{100}{1} \\ &= 6.978 \text{ hr} \times 2 \\ &= \mathbf{13.956 \text{ hr}} \end{aligned}$$

(ii) To calculate the volume of dry N_2O produced at STP

$$\begin{aligned} 1 \text{ mole of } \text{NH}_2\text{NO}_2 &= 1 \text{ mol of } \text{N}_2\text{O} \\ 62 \text{ g mol}^{-1} &= 22.4 \text{ lit at STP} \end{aligned}$$

$$\begin{aligned} 6.2 \text{ g} &= \frac{22.4 \times 6.2}{62} \\ &= 2.24 \text{ lit} \end{aligned}$$

volume of N_2O produced at STP when % decomposition is 99%

$$\begin{aligned} &= \frac{2.24 \times 99}{100} \text{ lit} \\ &= \mathbf{2.2176 \text{ lit}} \end{aligned}$$

SOLVED PROBLEM 33. At 380°C the half period for the first order decomposition of H_2O_2 is 360 minutes. The energy of activation of the reaction is 200 kJ mol^{-1} . Calculate the time required for 75% decomposition at 450°C .

SOLUTION :**Formula used**

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$$

Quantities given

$$\begin{aligned} k_1 &= \frac{0.693}{t_{1/2}} = \frac{0.693}{360 \text{ min}} = 1.925 \times 10^{-3} \text{ min}^{-1} & T_1 &= 380 + 273 = 653 \text{ K} \\ E_a &= 200 \text{ kJ mol}^{-1} & R &= 8.314 \text{ J K}^{-1} \text{ mol}^{-1} & T_2 &= 450 + 273 = 723 \text{ K} \end{aligned}$$

Substitution of values

$$\log \frac{16.2 \times 10^{-3} \text{ sec}^{-1}}{2.45 \times 10^{-5} \text{ sec}^{-1}} = \frac{200 \text{ kJ mol}^{-1}}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left[\frac{723 \text{ K} - 653 \text{ K}}{723 \text{ K} \times 653 \text{ K}} \right]$$

$$\begin{aligned} \text{or} \quad &= \frac{10.445 \times 70}{723 \times 653} \\ &= 0.01549 \end{aligned}$$

$$\text{or} \quad \frac{k_2}{1.925 \times 10^{-3}} = \text{Antilog} (0.00154) = 1.003573$$

$$\text{or} \quad k_2 = 1.925 \times 10^{-3} \text{ min}^{-1} \times 1.003573 = 1.931878 \times 10^{-3} \text{ min}^{-1}$$

(ii) To calculate time required for 75% decomposition of H_2O_2 at 450°C **Formula used**

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

Quantities given

$$k = 1.931878 \times 10^{-3} \text{ min}^{-1}$$

$$a = 100$$

$$x = 75$$

$$a - x = 100 - 75 = 25$$

Substitution of values

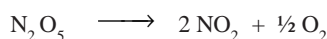
$$\begin{aligned} t &= \frac{2.303}{1.931878 \times 10^{-3} \text{ min}^{-1}} \log \frac{100}{25} \\ &= 717.76 \text{ min} \end{aligned}$$

ADDITIONAL PRACTICE PROBLEMS

1. The rate of formation of a dimer in a second order dimerisation reaction is $5.8 \times 10^{-3} \text{ mol lit}^{-1}$ at 0.10 mol monomer concentration. Calculate the value of rate constant.

Answer. $5.8 \times 10^{-3} \text{ mol lit}^{-1} \text{ sec}^{-1}$

2. The half life of the reaction



is 2.4 hours at 30 °C.

(a) Starting with 100 g of N_2O_5 how many grams will remain after a period of 9.6 hours ?

(b) What time would be required to reduce 5×10 moles of N_2O_5 to 10^8 molecules ?

Answer. (a) 6.25 g (b) 21.52 hrs

3. A reaction that is first order with respect to the reactant A has a rate constant of 6 min^{-1} . If we start $[A] = 5.0 \text{ mol lit}^{-1}$ when would $[A]$ reach the value of $0.05 \text{ mol lit}^{-1}$?

Answer. 0.7676 min

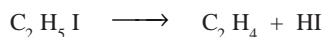
4. A first order reaction is 20% complete in 20 minutes. Calculate the time taken for the reaction to go to 80% completion.

Answer. 144.27 min

5. The rate constant of a first order reaction becomes 6 times when the temperature is increased from 350 K to 410 K, Calculate the energy of activation for the reaction ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

Answer. 35.656 k J

6. The reaction



is of first order and its rate constants are 3.20×10^{-4} at 600 K and $1.60 \times 10^{-2} \text{ sec}^{-1}$ at 1200 K. Calculate the energy of activation for the reaction. ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

Answer. 39.07 kJ

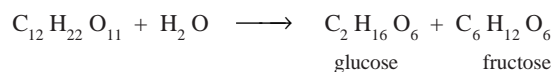
7. Find the two third life $t_{2/3}$ of a first order reaction in which $k = 5.48 \times 10^{-14} \text{ sec}^{-1}$.

Answer. $20 \times 10^{13} \text{ sec}$

8. For a certain reaction, it takes 5 minutes for the initial concentration of 0.5 mol lit^{-1} to become $0.25 \text{ mol lit}^{-1}$ and another 5 minutes to become $0.125 \text{ mol lit}^{-1}$. (a) What is the order of the reaction ? (b) What is the rate constant of the reaction ?

Answer. (a) One (b) 0.136 min^{-1}

9. For the inversion of cane sugar

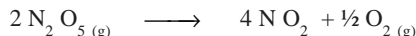


the second order rate constant is $2.12 \times 10^{-4} \text{ lit mol}^{-1} \text{ sec}^{-1}$ at 27 °C. The activation energy of the reaction is

$1.07 \times 10^5 \text{ mol}^{-1}$. What is the rate constant of the reaction at 37°C ?

Answer: $8.457 \times 10^{-4} \text{ lit mol}^{-1} \text{ sec}^{-1}$

10. The following reaction is first order with a rate constant of $4.80 \times 10^{-4} \text{ sec}^{-1}$ at 45°C .

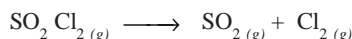


(a) If the initial concentration is $1.65 \times 10^{-2} \text{ mol lit}^{-1}$, calculate the concentration after 13.75 minutes.

(b) How long would it take for the concentration of N_2O_5 to decrease to $1.0 \times 10^{-2} \text{ mol lit}^{-1}$ from its initial value?

Answer: $0.0111 \text{ mol lit}^{-1}$; (b) 17.4 min

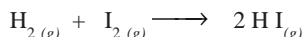
11. Sulphuryl chloride, SO_2Cl_2 , decomposes in a first order reaction according to the equation



The value of rate constant at 32°C is $2.2 \times 10^{-5} \text{ sec}^{-1}$. Calculate (a) half life period of SO_2Cl_2 at this temperature and (b) How long would it take for 75% of SO_2Cl_2 to decompose?

Answer: (a) $3.15 \times 10^4 \text{ sec}$; (b) 17.5 hours

12. The rate constant for the formation of hydrogen iodide according to the equation



is $2.7 \times 10^{-4} \text{ lit mol}^{-1} \text{ sec}^{-1}$ at 600 K and $3.5 \times 10^{-3} \text{ lit mol}^{-1} \text{ lit mol}^{-1} \text{ sec}^{-1}$ at 650 K. Calculate the energy of activation for the reaction.

Answer: $1.66 \times 10^5 \text{ J mol}^{-1}$

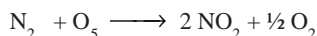
13. The rate of a particular reaction becomes three times when the temperature is increased from 298 K to 308 K. Calculate the energy of activation for the reaction.

Answer: 83.8 kJ mol^{-1}

14. A first order reaction takes 100 minutes for the completion of 60 percent of reaction. Find the time when 90 percent of the reaction will be completed.

Answer: 251.2 min

15. The reaction



is of first in N_2O_5 . Its rate constant is $6.2 \times 10^{-6} \text{ sec}^{-1}$. If in the beginning $[\text{N}_2\text{O}_5]$ is 15 mol lit^{-1} , calculate the rate of reaction in the beginning.

Answer: $9.3 \times 10^{-5} \text{ mol lit}^{-1} \text{ sec}^{-1}$

16. If the half life of a first order in A is 2 min, how long will it take A to reach 25% of its initial concentration.

Answer: 4 min

17. Calculate the half life of a first order reaction where the specific rate constant is (a) 200 sec^{-1} (b) 2 min^{-1} .

Answer: (a) 0.00346 sec^{-1} ; (b) 0.3465 min^{-1}

18. A first order reaction is found to have a rate constant $k = 7.39 \times 10^{-5} \text{ sec}^{-1}$. Calculate $t_{0.5\%}$ and $t_{0.80\%}$.

Answer: 21783.4 sec and 18763.68 sec

19. An acid solution of sucrose was hydrolysed to the extent of 54% after 67 minutes. Assuming the reaction to be of first order, calculate the time taken for 80% hydrolysis.

Answer: 124.4 min

20. A second order reaction in which both the reactants have the same concentration is 25% complete in 10 minutes. How long will it take for the reaction to go to 90% completion?

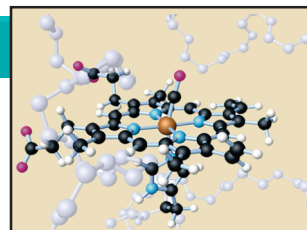
Answer: 2700 min

21

Catalysis

CHAPTER

KEY CONCEPTS AND EQUATIONS



CATALYST AND ITS TYPES

A catalyst is defined as a substance which alters the rate of a chemical reaction, itself remaining chemically unchanged at the reaction. This process is called catalysis. There are two main types of catalysis :

HOMOGENEOUS CATALYSIS

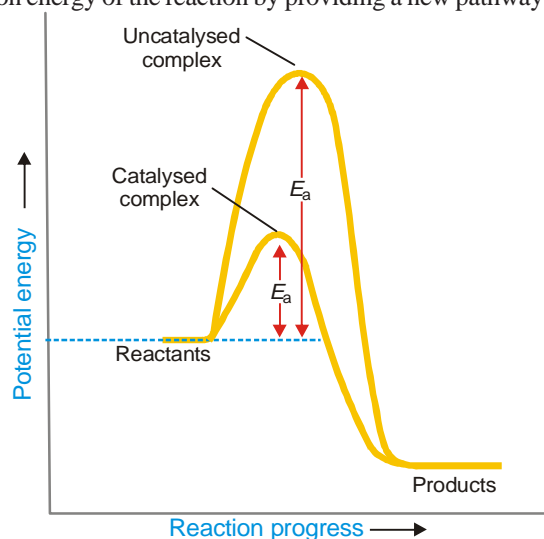
In homogeneous catalysis, the catalyst is in the same phase as the reactants and is evenly distributed throughout. This type of catalysis can occur in gas phase or the liquid (solution) phase.

HETEROGENEOUS CATALYSIS

In heterogeneous catalysis, the catalyst is in a different physical phase from the reactants.

ACTIVATION ENERGY AND CATALYSIS

Activation energy is defined as the minimum amount of energy required to cause a chemical reaction. A catalyst lowers the activation energy of the reaction by providing a new pathway as shown in Fig. 21.1.



■ **Figure 21.1**
Role of a catalyst.

ARRHENIUS EQUATION

Arrhenius suggested a simple relationship between the rate constant, k , for a reaction and the temperature of the system

$$k = A e^{-E_a/RT}$$

where E_a is the activation energy, R is the gas constant, T is absolute temperature and A is an experimentally determined quantity.

Taking natural logarithms, we have

$$\ln k = \frac{-E_a}{RT} + \ln A$$

or

$$\log k = \frac{-E_a}{2.303RT} + \log A$$

If k_1 and k_2 are the values of rate constants at temperature T_1 and T_2 , we have

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Arrhenius equation is used to calculate the activation energy, E_a , if the experimental value of rate constant, k is known.

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. In the Arrhenius equation for a certain reaction, the value of A and E_a (activation energy) are $4 \times 10^{13} \text{ sec}^{-1}$ and 98.6 kJ mol^{-1} respectively. If the reaction is of first order, at what temperature will its half life period be 10 minutes ?

SOLUTION : (i) To calculate the value of rate constant k

Formula used

$$k = \frac{0.693}{t_{1/2}}$$

Quantities given

$$t_{1/2} = 10 \text{ min} = 10 \times 60 \text{ sec} = 600 \text{ sec}$$

Substitution of values

$$k = \frac{0.693}{600 \text{ sec}} = 1.155 \times 10^{-3} \text{ sec}^{-1}$$

(ii) To calculate the temperature

Formula used

$$K = A e^{-E_a/RT}$$

Quantities given

$$\begin{array}{lll} k = 1.155 \times 10^{-3} \text{ sec}^{-1} & R = 8.314 \text{ J} & E_a = 98.6 \text{ kJ} \\ A = 4 \times 10^{13} \text{ sec}^{-1} & & = 98.6 \times 10^3 \text{ J} \end{array}$$

Substitution of values

$$\begin{aligned} \log (1.155 \times 10^{-3}) &= - \frac{98.6 \times 10^3 \text{ J}}{2.303 \times 8.314 \text{ J} \times T} + \log (4 \times 10^{13}) \\ - 2.9374 &= - \frac{5149.59}{T} + 13.6021 \\ - 16.5395 &= - \frac{5149.59}{T} \end{aligned}$$

or

$$T = \frac{5149.59}{16.5395}$$

$$= 311.35 \text{ K}$$

SOLVED PROBLEM 2. From the following data for the reaction between A and B

$2A \longrightarrow B$			
A (mol L ⁻¹)	B (mol L ⁻¹)	Initial rate at 300 K	Initial rate at 320 K
2.5×10^{-4}	3.0×10^{-5}	5.0×10^{-4}	2.0×10^{-3}
5.0×10^{-4}	6.0×10^{-5}	4.0×10^{-3}	—
1.0×10^{-3}	6.0×10^{-5}	1.0×10^{-2}	—

Calculate the energy of activation and the pre-exponential factor.

SOLUTION : (i) To calculate rate constants (k_1) at 300 K and (k_2) at 320 K**Formula used**

$$\text{Rate constant} = \frac{\text{Rate}}{[A]^2[B]}$$

Quantities given

$$\text{Rate at 300 K} = 5.0 \times 10^{-4}$$

$$\text{Rate at 320 K} = 2 \times 10^{-3}$$

$$[A] = 2.5 \times 10^{-4}$$

$$[B] = 3.0 \times 10^{-5}$$

Substitution of values

$$\begin{aligned} \text{Rate constant } k_1 \text{ at } 300 \text{ K} &= \frac{5.0 \times 10^{-4}}{(2.5 \times 10^{-4})^2 \times (3.0 \times 10^{-5})} \\ &= 2.66 \times 10^8 \end{aligned}$$

$$\begin{aligned} \text{Rate constant } k_2 \text{ at } 320 \text{ K} &= \frac{2 \times 10^{-3}}{(2.5 \times 10^{-4})^2 \times (3.0 \times 10^{-5})} \\ &= 1.066 \times 10^9 \end{aligned}$$

(ii) To calculate the energy of Activation.**Formula used**

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Quantities given

$$k_1 = 2.66 \times 10^8$$

$$k_2 = 1.066 \times 10^9$$

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$T_1 = 300 \text{ K}$$

$$T_2 = 320 \text{ K}$$

Substitution of values

$$\log \frac{1.066 \times 10^9}{2.66 \times 10^8} = \frac{E_a}{2.303 \times 8.314} \left[\frac{320 - 300}{320 \times 300} \right]$$

or

$$\begin{aligned} E_a &= \frac{0.6028 \times 2.303 \times 8.314 \times 320 \times 300}{20} \\ &= 5.5401 \times 10^4 \text{ J} \end{aligned}$$

(iii) To calculate pre-exponential factor**Formula used**

$$k = A e^{-E_a/RT}$$

or

$$\log k = \log A - \frac{E_a}{2.303 RT}$$

Quantities given

$$k = 2.66 \times 10^8$$

$$R = 8.314 \text{ J}$$

$$E_a = 5.5401 \times 10^4 \text{ J}$$

$$T = 300 \text{ K}$$

Substitution of values

$$\log 2.66 \times 10^8 = \log A - \frac{5.5401 \times 10^4}{2.303 \times 8.314 \times 300}$$

$$8.4249 = \log A - 9.6448$$

or

$$\log A = 18.6697$$

or

$$A = \text{Antilog } 18.6697$$

$$= 1.175 \times 10^{18}$$

SOLVED PROBLEM 3. At 380 °C, the half life period for the first order decomposition of H_2O_2 is 360 min. The rate constant at 450 °C is $6.81 \times 10^{-2} \text{ min}^{-1}$. Calculate the energy of activation of the reaction.

SOLUTION : (i) To calculate the rate constant k_1 at 380 °C**Formula used**

$$k_1 = \frac{0.693}{t_{1/2}}$$

Quantity given

$$t_{1/2} = 360 \text{ min}$$

Substitution of values

$$k_1 = \frac{0.693}{360 \text{ min}}$$

$$= 1.925 \times 10^{-3} \text{ min}^{-1}$$

(ii) To calculate the energy of activation**Formula used**

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

Quantities given

$$k_2 = 6.81 \times 10^{-2} \text{ min}^{-1}$$

$$T_2 = 450 + 273 = 723 \text{ K}$$

$$k_1 = 1.925 \times 10^{-3} \text{ min}^{-1}$$

$$T_1 = 380 + 273 = 653 \text{ K}$$

$$R = 8.314 \text{ J}$$

Substitution of values

$$\log \frac{6.81 \times 10^{-2}}{1.925 \times 10^{-3}} = \frac{E_a}{2.303 \times 8.314} \left[\frac{723 - 653}{723 \times 653} \right]$$

$$1.5487 = \frac{E_a}{2.303 \times 8.314} \times \frac{70}{723 \times 653}$$

or

$$E_a = 200000 \text{ J} = 200 \text{ kJ}$$

ADDITIONAL PRACTICE PROBLEMS

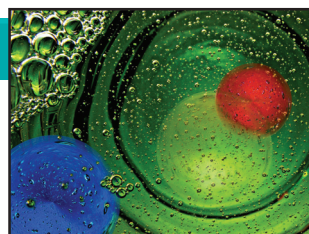
- For the reaction of hydrogen with iodine, the rate constant is $2.45 \times 10^{-4} \text{ lit mol}^{-1}$ at 302°C and $0.950 \text{ lit mol}^{-1}$ at 508°C . Calculate the activation energy and the frequency factor for this reaction.
Answer. 150 kJ , $9.93 \times 10^{-9} \text{ lit mol}^{-1}$
- The rate constants for the decomposition of SO_2Cl_2 is $6.09 \times 10^{-5} \text{ min}^{-1}$ at 552.3 K . Calculate the frequency factor and rate constant at 600 if its activation energy is 210 kJ .
Answer. $4.42 \times 10^{15} \text{ min}^{-1}$; $2.31 \times 10^{-3} \text{ min}^{-1}$
- The rate constant for the first order decomposition of ethyl bromide at 800 K and 900 K are 0.0361 and 1.410 sec^{-1} respectively. Calculate the activation energy for the reaction.
Answer. 219 kJ
- A first order reaction is half complete in 30 minutes at 300 K and in 10 minutes at 320 K . Calculate the reaction rate constant at 300 K and the energy of activation.
Answer. 0.0231 min^{-1} ; 43.848 kJ
- The specific reaction rate of a reaction is $1 \times 10^{-3} \text{ min}^{-1}$ at 300 K and $2 \times 10^{-3} \text{ min}^{-1}$ at 310 K . Calculate the energy of activation of the reaction.
Answer. 53.6 kJ
- The rate constant of a first order reaction is 6 times the rate constant when the temperature is increased from 350 K to 410 K . Calculate the energy of activation for the reaction.
Answer. 35.63 kJ
- The rate constants of a chemical reaction are $1 \times 10^{-3} \text{ sec}^{-1}$ and $2 \times 10^{-3} \text{ sec}^{-1}$ at 30°C and 40°C respectively. Calculate the energy of activation of the reaction.
Answer. 54.658 kJ
- The decomposition of a compound follows first order kinetics and specific rate constants are $5.5 \times 10^{-1} \text{ sec}^{-1}$ and $9.2 \times 10^{-3} \text{ sec}^{-1}$ at 413 K and 458 K respectively. Calculate the energy of activation.
Answer. $2.37 \times 10^4 \text{ cal}$
- Calculate the activation energy of a reaction for which the rate becomes double when the temperature is raised from 291 K to 311 K .
Answer. 50.80 kJ
- The specific reaction rate for a reaction increases by a factor of 4 if the temperature is raised from 27°C to 47°C . Calculate the activation energy of the reaction.
Answer. 55.693 kJ

22

The Colloids

CHAPTER

KEY CONCEPTS AND EQUATIONS



COLLOIDAL SOLUTIONS

A colloidal solution is an intermediate between true solution and suspension. In colloidal solution the size of the particle ranges from about 10 \AA to 2000 \AA .

LYOPHILIC AND LYOPHOBIC SOLS

Lyophilic sols are those in which the dispersed phase exhibits a definite affinity for the medium or the solvent.

Lyophobic sols are those in which the dispersed phase has no attraction for the medium or the solvent.

GOLD NUMBER

It is defined as the number of milligrams of a hydrophobic colloid that will just prevent the precipitation of 10 ml of a gold sol on the addition of 1 ml of 10 percent sodium chloride solution.

EMULSIONS AND THEIR TYPES

An emulsion may be defined as a dispersion of finely divided liquid droplets in another liquid. Emulsions are of two types

- (i) Oil in water type (O/W) and (ii) Water in oil type (W/O)

MACROMOLECULES

Colloidal solutions are formed by aggregation of atoms or molecules to give particles of colloidal size. There are substances which are composed of giant molecules and dissolve directly in a solvent to give colloidal solutions. Such giant molecules are called macromolecules.

MOLECULAR WEIGHT OF MACROMOLECULES

Two types of average molecular weights have been defined.

- (i) Number average molecular weight

$$\overline{M}_n = \frac{\sum n_i M_i}{\sum n_i}$$

where $n_i M_i$ stands for the weight of macromolecules numbering n_i and having molecular weight M_i

(ii) Weight average molecular weight

$$\overline{M}_w = \frac{\sum m_i M_i}{m_i}$$

where m_i represent the mass of macromolecules having molecular weight M_i .

These two molecular weights are compared as follows :

$$\overline{M}_w > \overline{M}_n$$

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. Consider a polymer mixture composed of 5 molecules of molar mass 1 kg mol⁻¹, 5 molecules of molar mass 2 kg mol⁻¹, 5 molecules of molar mass 3 kg mol⁻¹ and 5 molecules of molar mass 4 kg mol⁻¹. Calculate (i) the number average molecular weight and (ii) weight average molecular weight.

SOLUTION : (i) To calculate the number average molecular weight

Formula used

$$\overline{M}_n = \frac{\sum n_i M_i}{\sum n_i} = \frac{n_1 M_1 + n_2 M_2 + n_3 M_3 + n_4 M_4}{n_1 + n_2 + n_3 + n_4}$$

Quantities given

$$\begin{array}{llll} M_1 = 1 \text{ kg mol}^{-1} & M_2 = 2 \text{ kg mol}^{-1} & M_3 = 3 \text{ kg mol}^{-1} & M_4 = 4 \text{ kg mol}^{-1} \\ n_1 = 5 & n_2 = 5 & n_3 = 5 & n_4 = 5 \end{array}$$

Substitution of values

$$\begin{aligned} \overline{M}_n &= \frac{1 \times 5 + 2 \times 5 + 3 \times 5 + 4 \times 5}{5 + 5 + 5 + 5} \text{ kg mol}^{-1} \\ &= \frac{5 + 10 + 15 + 20}{20} \text{ kg mol}^{-1} \\ &= 2.5 \text{ kg mol}^{-1} \end{aligned}$$

(ii) To calculate the weight average molecular weight

Formula used

$$\overline{M}_w = \frac{\sum m_i M_i}{\sum m_i} = \frac{w_1 M_1 + w_2 M_2 + w_3 M_3 + w_4 M_4}{m_1 + m_2 + m_3 + m_4}$$

Quantities gives

$$\begin{array}{llll} M_1 = 1 \text{ kg mol}^{-1} & M_2 = 2 \text{ kg mol}^{-1} & M_3 = 3 \text{ kg mol}^{-1} & M_4 = 4 \text{ kg mol}^{-1} \\ m_1 = 1 & m_2 = 2 & m_3 = 3 & m_4 = 4 \end{array}$$

Substitution of values

$$\begin{aligned} \overline{M}_w &= \frac{1 \times 1 + 2 \times 2 + 3 \times 3 + 4 \times 4}{1 + 2 + 3 + 4} \text{ kg mol}^{-1} \\ &= \frac{30}{10} \text{ kg mol}^{-1} \\ &= 3 \text{ kg mol}^{-1} \end{aligned}$$

SOLVED PROBLEM 2. A sample of polymer contains 10, 20, 30 and 40 percent molecules of the polymer with molecular weights 10000, 12000, 14000 and 16000. Calculate the mole fraction of each type of polymer molecule. Also calculate the number and weight average molecular weights of the polymer sample.

SOLUTION : (i) To calculate the mole fraction of each type of polymer**Formula used**

$$\text{Mole fraction } \overline{X}_i = \frac{\text{Number of molecules of type } i}{\text{Total number of molecules}}$$

Quantities given

No. of molecules of each type = 10, 20, 30 and 40

Total number of molecules = 100

Substitution of values

$$\text{Mole fraction of type A} = \frac{10}{100} = 0.1$$

$$\text{Mole fraction of type B} = \frac{20}{100} = 0.2$$

$$\text{Mole fraction of type C} = \frac{30}{100} = 0.3$$

$$\text{Mole fraction of type D} = \frac{40}{100} = 0.4$$

(ii) To calculate the number average molecular weight**Formula used**

$$\overline{M}_n = \frac{\sum n_i M_i}{\sum n_i}$$

Quantities given

$$n_1 = 0.1$$

$$n_2 = 0.2$$

$$n_3 = 0.3$$

$$n_4 = 0.4$$

$$M_1 = 10000$$

$$M_2 = 12000$$

$$M_3 = 14000$$

$$M_4 = 16000$$

Substitution of values

$$\begin{aligned} \overline{M}_n &= \frac{0.1 \times 10000 + 0.2 \times 12000 + 0.3 \times 14000 + 0.4 \times 16000}{0.1 + 0.2 + 0.3 + 0.4} \\ &= 1000 + 2400 + 4200 + 6400 \\ &= 14000 \end{aligned}$$

(iii) To calculate the weight average molecular weight.**Formula used**

$$\begin{aligned} \overline{M}_w &= \frac{\sum X_i M_i^2}{\sum M_i} \\ &= \frac{0.1 \times (10000)^2 + 0.2 \times (12000)^2 + 0.3 \times (14000)^2 + 0.4 \times (16000)^2}{14000} \\ &= \frac{10^7 + 2.88 \times 10^7 + 5.88 \times 10^7 + 10.24 \times 10^7}{14000} \\ &= \frac{20 \times 10^7}{14000} \\ &= 14286 \end{aligned}$$

ADDITIONAL PRACTICE PROBLEMS

1. The following distribution of molecular weights has been found in a polymer sample

n_i	5	10	10	10	20	5	5
M_i	1000	2000	5000	10000	12000	15000	20000

Calculate the number average weight of the polymer.

Answer. 19461

2. A sample of polymer contain 5, 25, 40, and 30 percent molecules of the polymer with molecular weights 5000, 6000, 7000, and 8000. What is the mole fraction of each type of polymer ? Also calculate the number average molecular weight of polymer sample.

Answer. 0.05, 0.025, 0.40 and 0.3 ; 6950

3. A sample of polymer contains 100 molecules having molecular weight 10^3 each and 200 molecules with molecular weight 10^4 each and 200 molecules with molecular weight 10^5 each, Calculate the number average and weight average molecular weight.

Answer. 44000, 91000

4. Calculate the weight average molecular weight of a polymer containing equal number of particles with molecular weights 5000 and 10000.

Answer. 8333

5. Calculate number average molecular weight of a given sample of a polymer having 1000 molecules of 5000, 500 molecules of 4000 and 200 molecules of 3000 molecular weights.

Answer. 4470

6. A suspension contains equal masses of particles with molecular weight 20,000 and 40,000. Calculate number and weight average molecular weights of the suspension.

Answer. 26,667 and 30,000

7. There are two polymers A and B. A consists of equal number of molecular masses 10,000 and 30,000. B consists of equal number of molecular masses 15,000 and 35,000. Calculate the number average and mass average molecular mass for each polymer.

Answer. 20,000 and 25,000 ; 25,000 and 29,000

8. A sample of polymer contains 0.5 mole fraction with molecular weight 100,000 and 0.5 mole fraction with molecular weight 200,000. Calculate the average molecular weight of the polymer.

Answer. 150,000 and 166,667

9. Calculate the number average molecular weight of a sample of nylon having 1000 molecules of 5000 ; 2000 molecules of 6000 and 4000 molecules of 1000 molecular weight.

Answer. 3000

10. Calculate weight average molecular weight of a sample containing equal number of particles with molecular weight 10,000 and 20,000.

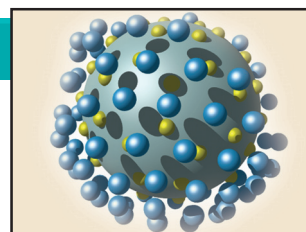
Answer. 16667

23

Adsorption

CHAPTER

KEY CONCEPTS AND EQUATIONS



ADSORPTION

The phenomenon of concentration of molecules of a gas or liquid at a solid surface is called adsorption.

PHYSICAL ADSORPTION

It is due to the gas molecules being held to the solid surface by vander Waal's attractive forces.

CHEMICAL ADSORPTION

It is due to the gas molecules being held to the solid surface by chemical bonds.

ADSORPTION ISOTHERMS

The relationship between the equilibrium pressure and its amount absorbed on the solid adsorbent at any constant temperature is called an Adsorption Isotherm.

FREUNDLICH ADSORPTION ISOTHERM

The relation between the amount of gas adsorbed and its pressure is

$$w/m = kp^{1/n}$$

where w is the mass of the gas adsorbed on a mass m of adsorbent at a pressure p , k and n are constants depending upon the nature of the gas and adsorbent and on temperature.

LANGMUIR ADSORPTION ISOTHERM

The relation between the amount of gas adsorbed and its pressure is also given by

$$x = K' \frac{KP}{1 + KP}$$

where K' is a constant, K is adsorption constant and P is the pressure of the gas.

Langmuir adsorption isotherm holds good at low pressures but fails at high pressures.

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. 2.5 g of oxygen is adsorbed on 1.5 g of metal powder at 27 °C and 0.7 atm.

Express the mass, number of moles and volume of oxygen at 27 °C, 0.7 atm and at NTP adsorbed per gram of the adsorbent.

SOLUTION :

$$\begin{aligned}
 \text{Mass of adsorbate} &= 2.5 \text{ g} \\
 \text{Mass of adsorbent} &= 1.5 \text{ g} \\
 \text{Mass of adsorbate per gram of adsorbent} &= \frac{2.5 \text{ g}}{1.5 \text{ g}} = \mathbf{1.67} \\
 \text{Number of moles of adsorbate per gram of adsorbent} &= \frac{1.67}{32} = \mathbf{0.052} \\
 \text{Volume of 1.67 g of O}_2 \text{ at 27 }^\circ\text{C and 0.7 atm} &= \frac{0.052 \times 82 \times 300}{0.7} \\
 &= \mathbf{1827.4 \text{ ml}} \\
 \text{Volume of 1.67 g of O}_2 \text{ at 273 K and 1 atm} &= \frac{0.052 \times 82 \times 273}{0.7} \\
 &= \mathbf{1662.9 \text{ ml}}
 \end{aligned}$$

SOLVED PROBLEM 2. The adsorption of a gas on a metal powder obeys Langmuir equation. The following experimental results have been obtained.

p (torr)	1	5	10	30	70	150
x/m	0.75	1.50	1.71	1.89	1.95	1.98

Determine the parameters a and b of the Langmuir equation.

SOLUTION : (i) To calculate the value of m/x and $1/p$.

m/x	1.333	0.666	0.585	0.529	0.513	0.505
$1/p$ (torr $^{-1}$)	1	0.2	0.1	0.033	0.014	0.0066

On plotting m/x against $1/p$, we get a straight line whose slope is 0.83 torr and intercept = 0.5.

(ii) To calculate the value of a and b

$$\begin{aligned}
 \text{Thus} \quad 1/a &= 0.83 \text{ torr} \quad \text{or} \quad a = \mathbf{1.2 \text{ torr}^{-1}} \\
 b/a &= 0.5 \quad \text{and} \quad b = \mathbf{0.6 \text{ torr}^{-1}}
 \end{aligned}$$

ADDITIONAL PRACTICE PROBLEMS

- 4 g of a substance absorbs 87.5 ml of O_2 at 450 torr at 37°C . Calculate x/m in mol per gram.
Answer. $5.265 \times 10^{-4} \text{ mol g}^{-1}$
- 100 ml of 0.3 M acetic acid is shaken with 0.8 g of wood charcoal. The final concentration of the solution after adsorption is 0.125 M. Calculate the weight of acetic acid adsorbed per gram of carbon.
Answer. 1.31 g
- Five grams of a catalyst absorb 400 cm^3 of N_2 at STP to form a monolayer. What is the surface area per gram if the area occupied by a molecule of N_2 is 16 \AA .
Answer. $344 \text{ m}^2 \text{ g}^{-1}$
- Charcoal absorbs a solute from its aqueous solution and obeys the Freundlich isotherm. The following data were obtained :

Equilibrium Conc $\times 10^2 M$	2.0	4.0	6.0	8.0
x/m	0.185	0.290	0.364	0.428

 Determine the values of k and n .
Answer. $k = 206$; $n = 0.616$

5. Four gram of a gas is adsorbed on 1.5 g of metal powder at 300 K and 0.7 atm. Calculate the volume of the gas at STP adsorbed per gram of adsorbent.

Answer. 2052.5 m

6. 10.0 g of oxygen is adsorbed on 2.5 g of metal powder at 273 K and 1 atm pressure. Calculate the volume of the gas adsorbed per gram of adsorbent.

Answer. 2798.25 ml

7. For an adsorbent – adsorbate system obeying the Langmuir adsorption isotherm, $a = 0.48 \text{ bar}^{-1}$ and $b = 0.16 \text{ bar}^{-1}$. At what pressure will 50 % of the surface be covered ?

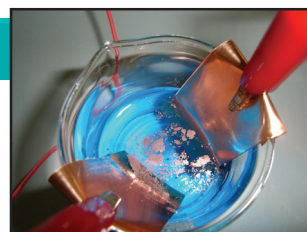
Answer. 1.25 bar

24

Electrolysis and Electrical Conductance

CHAPTER

KEY CONCEPTS AND EQUATIONS



ELECTROLYSIS AND ELECTRICAL UNITS

The phenomenon of decomposition of an electrolyte by passing electric current through its solution is called Electrolysis. On passing electric current the ions move towards the oppositely charged electrodes where they get discharged either by losing electron or by gaining electrons. As a result of this chemical reaction takes place.

Coulomb

It is a unit of quantity of electricity. When 1 ampere current is passed for one second, the quantity of electricity is called one coulomb.

Ampere

It is a unit rate of flow of electricity. It is that current which will deposit 0.00118 g of silver in one second.

FARADAY'S LAWS OF ELECTROLYSIS

First law

The amount of a given substance liberated at an electrode during electrolysis is directly proportional to the quantity of electricity which passes through the electrolyte solution *i.e.*

$$\begin{aligned} m &\propto Q \\ \text{or} \quad m &\propto I \times t & [\because Q = I \times t] \\ \text{or} \quad m &= Z \times I \times t \end{aligned}$$

where m is the mass of substance deposited in grams, I the strength of current in amperes, t the time in seconds for which the current has been passed and Z is a constant called Electrochemical equivalent.

$$\begin{aligned} \text{If} \quad I &= 1 \text{ ampere, } t = 1 \text{ second, then} \\ m &= Z \end{aligned}$$

Thus the electrochemical equivalent is the amount of a substance deposited by 1 ampere current passing for 1 second (*i.e.* one coulomb). The quantity of electricity required to liberate one gram equivalent of a substance is called Faraday, denoted by F and $1 F = 96500$ coulombs.

Second law

When the same quantity of electricity passes through solution of different electrolytes, the amounts of substances liberated at the electrodes are directly proportional to their chemical equivalents (equivalent weight). *i.e.*

$$\frac{\text{mass of substances A deposited}}{\text{mass of substances B deposited}} = \frac{\text{Eq.Wt. of substance A}}{\text{Eq. Wt. of substance B}}$$

CONDUCTANCE OF ELECTROLYTES

The solution of electrolytes conduct electricity by the movement of ions to oppositely charged electrodes on passing electric current. The power of electrolytes to conduct electrical current is called conductivity or conductance. Electrolytes obey Ohm's law like metallic conductors. According to this law, the current I flowing through a metallic conductor is given by

$$I = \frac{E}{R}$$

where E is the potential difference at two ends and R is the resistance measured in ohms (Ω). The resistance of a conductor is proportional to its length, l , and inversely proportional to its area of cross-section, A . That is

$$R \propto \frac{l}{A}$$

$$\text{or} \quad R = \rho \times \frac{l}{A}$$

where ρ "rho" is a constant of proportionality and is called resistivity or specific resistance. We can also write

$$\rho = R \times \frac{A}{l}$$

If $l = 1 \text{ cm}$, $A = 1 \text{ sq cm}$ then

$$\rho = R$$

Thus the specific resistance of a conductor is the resistance in ohms which one centimeter cube of it offers to the passage of electricity.

Specific conductance and its units

The reciprocal of specific resistance is called specific conductance or specific conductivity. It is defined as the conductance of one centimeter cube of a solution of an electrolyte. It is denoted by κ (Kappa). The

$$\begin{aligned} \kappa &= \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{A} \\ &= \frac{1}{\text{ohm}} \times \frac{\text{cm}}{\text{cm}^2} = \text{ohm}^{-1}\text{cm}^{-1} \end{aligned}$$

Equivalent conductance and its units

It is the conductance of an electrolyte by dissolving one gram-equivalent of it in $V \text{ cm}^3$ of water. It is denoted by Λ . It is equal to the product of the specific conductance κ and the volume in cm^3 containing 1 gram-equivalent of the electrolyte at the dilution V . Thus

$$\Lambda = \kappa \times V$$

If an electrolyte contains N grams equivalents in 1000 cm^3 of the solution, the volume containing 1 g-equivalent will be $1000/N$. Thus

$$\begin{aligned}\Lambda &= \frac{\kappa \times 1000}{N} \\ &= \kappa \times \frac{1000}{N} \\ &= \frac{1}{R} \times \frac{l}{A} \times V \quad \left[\because \kappa = \frac{1}{R} \times \frac{l}{A} \right] \\ &= \frac{1}{\text{ohm}} \times \frac{\text{cm}}{\text{cm}^2} \times \frac{\text{cm}^3}{\text{g eqvt}} \\ &= \text{ohm}^{-1} \text{ cm}^2 \text{ g eqvt}^{-1}\end{aligned}$$

Molar conductance and its units

The conductance of all ions produced by one mole of an electrolyte when dissolved in a certain volume $V \text{ cm}^3$. It is denoted by μ and is given by

$$\mu = \kappa \times V$$

where V is the volume of the solution in cm^3 containing 1 mole of the electrolyte.

$$\begin{aligned}\mu &= \frac{1}{R} \times \frac{l}{A} \times V \quad \left[\because \kappa = \frac{1}{R} \times \frac{l}{A} \right] \\ &= \frac{1}{\text{ohm}} \times \frac{\text{cm}}{\text{cm}^2} \times \frac{\text{cm}^3}{\text{mol}} \\ &= \text{ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}\end{aligned}$$

Degree of Dissociation

The degree of dissociation of a weak electrolyte is given by the conductance ratio *i.e.*

$$\alpha = \frac{\Lambda}{\Lambda_{\infty}}$$

where Λ is the equivalent conductance at a given concentration and Λ_{∞} is the equivalent conductance at zero concentration (infinite dilution).

Cell constant and its units

The ratio l/a is called the cell constant *i.e.*

$$\begin{aligned}\text{cell constant} &= \frac{l}{a} \\ &= \frac{\text{cm}}{\text{cm}^2} = \text{cm}^{-1}\end{aligned}$$

The cell constant is related in the specific conductance by the relation

$$\begin{aligned}\kappa &= \frac{1}{R} \times \text{cell constant} \\ \text{or} \quad \text{cell constant} &= \frac{\text{Specific conductance}}{\text{Observed conductance}}\end{aligned}$$

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. 0.5 normal solution of a salt placed between two platinum electrodes, 20 cm apart and of area of cross-section 4.0 sq cm has a resistance of 25 ohms. Calculate the equivalent conductance of the solution.

SOLUTION : (i) To calculate specific conductance**Formula used**

$$\kappa = \frac{1}{R} \times \frac{l}{a}$$

Quantities given

$$R = 25 \text{ ohms}$$

$$l = 20 \text{ cm}$$

$$a = 4.0 \text{ sq cm}$$

Substitution of values

$$\begin{aligned}\kappa &= \frac{1}{25 \text{ ohms}} \times \frac{20 \text{ cm}}{4.0 \text{ sq cm}} \\ &= 0.2 \text{ ohm}^{-1} \text{ cm}^{-1}\end{aligned}$$

(ii) To calculate equivalent conductance**Formula used**

$$\text{Equivalent conductance} = \frac{\kappa \times 1000}{N}$$

Quantities given

$$\kappa = 0.2 \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$N = 0.5 \text{ eqvt}$$

Substitution of values

$$\begin{aligned}\text{Equivalent conductance} &= \frac{0.2 \text{ ohm}^{-1} \text{ cm}^{-1} \times 1000 \text{ cm}^3}{0.5 \text{ eqvt}} \\ &= 400 \text{ ohm}^{-1} \text{ cm}^2 \text{ eqvt}^{-1}\end{aligned}$$

SOLVED PROBLEM 2. The resistance of N/10 solution is found to be 2.5×10^3 ohms. Calculate the equivalent conductance of the solution. Cell constant = 1.15 cm^{-1}

SOLUTION : To calculate specific conductance**Formula used**

$$\kappa = \frac{l}{R} \times \text{cell constant}$$

Quantities given

$$R = 2.5 \times 10^3 \text{ ohms}$$

$$\text{cell constant} = 1.15 \text{ cm}^{-1}$$

Substitution of values

$$\begin{aligned}\kappa &= \frac{1}{2.5 \times 10^3 \text{ ohm}} \times 1.15 \text{ cm}^{-1} \\ &= 4.60 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}\end{aligned}$$

(ii) To calculate equivalent conductance**Formula used**

$$\text{Equivalent conductance} = \frac{\kappa \times 1000}{N}$$

Quantities given

$$\kappa = 4.60 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$N = 0.1 \text{ eqvt}^{-1}$$

Substitution of values

$$\begin{aligned}\text{Equivalent conductance} &= \frac{4.60 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1} \times 1000 \text{ cm}^3}{0.1 \text{ eqvt}^{-1}} \\ &= 4.60 \text{ ohm}^{-1} \text{ cm}^2 \text{ eqvt}^{-1}\end{aligned}$$

SOLVED PROBLEM 3. In a particular cell, 0.01M solution of KCl gave a resistance of 15.0 ohm at 298 K while 0.01 M solution of HCl gave a resistance of 51.4 ohm at the same temperature. If the specific conductance of 0.01 M KCl is 0.1409 Sm^{-1} at 280 K, calculate the cell constant, specific conductance and equivalent conductance of the HCl solution.

SOLUTION : (i) To calculate cell constant

Formula used

$$\text{Cell constant} = \frac{\text{Specific conductance of KCl solution}}{\text{Observed conductance of KCl solution}}$$

Quantities given

$$\text{Specific conductance of KCl} = 0.1409 \text{ sm}^{-1}$$

$$\text{Observed conductance of KCl} = \frac{1}{\text{Resistance}} = \frac{1}{15 \text{ ohm}} = 0.0667 \text{ ohm}^{-1}$$

Substitution of values

$$\text{Cell constant} = \frac{0.1409 \text{ sm}^{-1}}{0.0667 \text{ ohm}^{-1}} = 2.11 \text{ cm}^{-1}$$

(ii) To calculate the specific conductance of 0.01 M HCl

Formula used

$$\text{Specific conductance} = \frac{1}{R} \times \text{cell constant}$$

Quantities given

$$R = 51.4 \text{ ohm}$$

$$\text{cell constant} = 2.11 \text{ cm}^{-1}$$

Substitution of values

$$\text{Specific conductance} = \frac{1}{51.4 \text{ ohm}} \times 2.11 \text{ cm}^{-1} = 4.10 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$$

(iii) To calculate the equivalent conductance of 0.01 M HCl

Formula used

$$\text{Equivalent Conductance} = \frac{\text{Specific conductance} \times 1000}{N}$$

Quantities given

$$\text{Specific Conductance} = 4.10 \times 10^{-2}$$

$$N = 0.01 \text{ eqvt}$$

Substitution of values

$$\begin{aligned} \text{Equivalent conductance} &= \frac{4.10 \times 10^{-2} \times 1000 \text{ cm}^3}{0.01 \text{ eqvt}} \\ &= 41 \text{ ohm}^{-1} \text{ cm}^2 \text{ eqvt}^{-1} \end{aligned}$$

SOLVED PROBLEM 4. The specific conductance of N/5 KCl solution at 25 °C is 0.002780 mho. The resistance of the cell containing this solution is 500 ohm. Calculate the cell constant.

SOLUTION :

Formula used

$$\text{Specific conductance} = \frac{1}{R} \times \text{cell constant}$$

or

$$\text{Cell constant} = \text{Specific conductance} \times \text{Resistance}$$

Quantities given

$$\text{Specific conductance} = 0.002780 \text{ mho}$$

$$R = 500 \text{ ohm}$$

Substitution of values

$$\begin{aligned}\text{Cell constant} &= 0.002780 \text{ mho} \times 500 \text{ ohm} \\ &= \mathbf{1.39}\end{aligned}$$

SOLVED PROBLEM 5. If the equivalent conductance at infinite dilution of NaCl, HCl and CH_3COONa are 126.45, 426.16 and 91.0 ohm^{-1} respectively, find the equivalent conductance of acetic acid at infinite dilution.

SOLUTION :**Formula used**

$$\lambda_{\infty}(\text{CH}_3\text{COOH}) = \lambda_{\infty}(\text{HCl}) + \lambda_{\infty}(\text{CH}_3\text{COONa}) - \lambda_{\infty}(\text{NaCl})$$

Quantities given

$$\lambda_{\infty}(\text{HCl}) = 426.16 \text{ ohm}^{-1} \quad \lambda_{\infty}(\text{CH}_3\text{COONa}) = 91.0 \text{ ohm}^{-1} \quad \lambda_{\infty}(\text{NaCl}) = 126.45 \text{ ohm}^{-1}$$

Substitution of values

$$\begin{aligned}\lambda_{\infty}(\text{CH}_3\text{COOH}) &= 426.16 \text{ ohm}^{-1} + 91.0 \text{ ohm}^{-1} - 126.45 \text{ ohm}^{-1} \\ &= \mathbf{390.71 \text{ ohm}^{-1}}\end{aligned}$$

SOLVED PROBLEM 6. The equivalent conductance of ammonium chloride at infinite dilution is 149.7 ; for sodium hydroxide it is 247.8 mho ; and for sodium chloride is 126.45 mho at 25°C . Calculate the equivalent conductance at the same temperature.

SOLUTION :**Formula used**

$$\lambda_{\infty}(\text{NH}_4\text{OH}) = \lambda_{\infty}(\text{NH}_4\text{Cl}) + \lambda_{\infty}(\text{NaOH}) - \lambda_{\infty}(\text{NaCl})$$

Quantities given

$$\lambda_{\infty}(\text{NH}_4\text{Cl}) = 149.7 \text{ mho} \quad \lambda_{\infty}(\text{NaOH}) = 247.8 \text{ mho} \quad \lambda_{\infty}(\text{NaCl}) = 126.45 \text{ mho}$$

Substitution of values

$$\begin{aligned}\lambda_{\infty}(\text{NH}_4\text{OH}) &= 149.7 \text{ mho} + 247.8 \text{ mho} - 126.45 \text{ mho} \\ &= \mathbf{271.05 \text{ mho}}\end{aligned}$$

SOLVED PROBLEM 7. The resistance of a 0.5 N solution of an electrolyte occupying a volume between two platinum electrodes which are 1.72 cm apart and have an area of 4.5 sq cm is 25 ohms . Calculate the equivalent conductance of the solution.

SOLUTION : (i) To calculate specific conductance**Formula used**

$$\text{Specific conductance} = \frac{1}{R} \times \frac{l}{a}$$

Quantities given

$$R = 25 \text{ ohm} \quad l = 1.72 \text{ cm} \quad a = 4.5 \text{ sq cm}$$

Substitution of values

$$\begin{aligned}\text{Specific conductance} &= \frac{1}{25 \text{ ohm}} \times \frac{1.72 \text{ cm}}{4.5 \text{ sq cm}} \\ &= 0.015289 \text{ ohm}^{-1}\text{cm}^{-1}\end{aligned}$$

(ii) To calculate equivalent conductance**Formula used**

$$\text{Equivalent conductance} = \frac{\text{Specific conductance} \times 1000}{N}$$

Quantities given

$$\text{Specific conductance} = 0.015289 \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$N = 0.5 \text{ eqvt}$$

Substitution of values

$$\begin{aligned} \text{Equivalent conductance} &= \frac{0.015289 \text{ ohm cm}^{-1} \times 1000 \text{ cm}^3}{0.5 \text{ eqvt}} \\ &= \mathbf{30.57 \text{ ohm cm}^2 \text{ eqvt}^{-1}} \end{aligned}$$

SOLVED PROBLEM 8. Following results were obtained by conductance measurements of potassium sulphate using the cell with cell constant 0.2281. The observed conductance of potassium sulphate solution is 3×10^{-3} mhos. The equivalent conductance of potassium sulphate solution is 140 mho cm^2 . Calculate the concentration of potassium sulphate solution..

SOLUTION : (i) To calculate the specific conductance**Formula used**

$$\text{Cell constant} = \frac{\text{Specific conductance}}{\text{Observed conductance}}$$

Quantities given

$$\text{Cell constant} = 0.2281$$

$$\text{Observed conductance} = 3 \times 10^{-3} \text{ mhos}$$

Substitution of values

$$0.2281 = \frac{\text{Specific conductance}}{3 \times 10^{-3} \text{ mho}}$$

$$\begin{aligned} \text{or Specific Conductance} &= 3 \times 10^{-3} \text{ mho} \times 0.2281 \\ &= 0.6843 \times 10^{-3} \text{ mho} \end{aligned}$$

(ii) To calculate concentration of the potassium sulphate solution**Formula used**

$$\text{Equivalent conductance} = \frac{\text{Specific conductance} \times 1000}{N}$$

Quantities given

$$\text{Specific conductance} = 0.6843 \times 10^{-3} \text{ mho}$$

$$\text{Equivalent conductance} = 140 \text{ mhos cm}^2$$

Substitution of values

$$140 \text{ mhos cm}^2 \text{ eqvt}^{-1} = \frac{0.6843 \times 10^{-3} \text{ mho} \times 1000 \text{ cm}^3}{N}$$

$$\text{or } N = \frac{0.6843 \times 10^{-3} \times 1000}{140} \text{ eqvt}$$

$$= \mathbf{0.00488 \text{ eqvt}}$$

SOLVED PROBLEM 9. 0.1 N solution of sodium acetate was placed between two electrodes which were 0.72 cm apart and each has a cross-section 2.25 cm^2 . The resistance of solution was 52.40 ohms. Find the specific and equivalent conductance.

SOLUTION : (i) To calculate the specific conductance**Formula used**

$$\text{Specific conductance} = \frac{1}{R} \times \frac{l}{a}$$

Quantities given

$$R = 52.40 \text{ ohm}$$

$$l = 0.72 \text{ cm}$$

$$a = 2.25 \text{ cm}^2$$

Substitution of values

$$\text{Specific conductance} = \frac{1}{52.40 \text{ ohm}} \times \frac{0.72 \text{ cm}}{2.25 \text{ cm}^2} = \mathbf{0.0061 \text{ ohm}^{-1} \text{ cm}^{-1}}$$

(ii) To calculate the equivalent conductance**Formula used**

$$\text{Equivalent conductance} = \frac{\text{Specific conductance} \times 1000}{N}$$

Quantities given

$$\text{Specific conductance} = 0.0061 \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$N = 0.1 \text{ eqvt}$$

Substitution of values

$$\begin{aligned} \text{Equivalent conductance} &= \frac{0.0061 \text{ ohm}^{-1} \text{ cm}^{-1} \times 1000 \text{ cm}^3}{0.1 \text{ eqvt}} \\ &= 61 \text{ ohm}^{-1} \text{ cm}^2 \text{ eqvt}^{-1} \end{aligned}$$

SOLVED PROBLEM 10. 0.5 N NaCl is placed between two electrodes 1.5 cm apart and having an area of each 3.0 sq cm offered a resistance of 25.0 ohms. Calculate the equivalent conductance.

SOLUTION : (i) To calculate the specific conductance**Formula used**

$$\text{Specific conductance} = \frac{1}{R} \times \frac{l}{a}$$

Quantities given

$$R = 25.0 \text{ ohm}$$

$$l = 1.5 \text{ cm}$$

$$a = 3.0 \text{ sq cm}$$

Substitution of values

$$\begin{aligned} \text{Specific conductance} &= \frac{1}{25.0 \text{ ohm}} \times \frac{1.5 \text{ cm}}{3.0 \text{ cm}^2} \\ &= 0.020 \text{ ohm}^{-1} \text{ cm}^{-1} \end{aligned}$$

(ii) To calculate the equivalent conductance**Formula used**

$$\text{Equivalent conductance} = \frac{\text{Specific conductance} \times 1000}{N}$$

Quantities given

$$\text{Specific conductance} = 0.020 \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$N = 0.5 \text{ eqvt}$$

Substituting of values

$$\begin{aligned} \text{Equivalent conductance} &= \frac{0.020 \text{ ohm}^{-1} \text{ cm}^{-1} \times 1000 \text{ cm}^3}{0.5 \text{ eqvt}} \\ &= 40 \text{ ohm}^{-1} \text{ cm}^2 \text{ eqvt}^{-1} \end{aligned}$$

SOLVED PROBLEM 11. A conductance cell when filled with 0.05 solution of KCl records a resistance of 410.5 ohm at 25 °C. When filled with calcium chloride solution (11 g CaCl_2 in 500 ml) it records 990 ohms. If the specific conductance of 0.05M KCl solution is $0.00189 \text{ mho cm}^{-1}$, calculate (i) the cell constant, (ii) specific conductance (iii) molecular conductance of CaCl_2 .

SOLUTION : (i) To calculate the cell constant**Formula used**

$$\text{Cell constant} = \frac{\text{Specific conductance}}{\text{Observed conductance}}$$

Quantities given

$$\text{Specific conductance} = 0.00189 \text{ mho cm}^{-1}$$

$$\text{Observed conductance} = \frac{1}{R} = \frac{1}{410.5 \text{ ohm}}$$

Substitution of values

$$\text{Cell constant} = \frac{0.00189 \text{ mho cm}^{-1}}{1/410.5 \text{ ohm}} = 0.7758 \text{ cm}^{-1}$$

(ii) To calculate specific conductance of CaCl_2 Solution**Formula used**

$$\text{Specific conductance} = \frac{1}{R} \times \text{cell constant}$$

Quantities given

$$R = 990 \text{ ohm}$$

$$\text{cell constant} = 0.7758 \text{ cm}^{-1}$$

Substitution of values

$$\begin{aligned} \text{Specific conductance} &= \frac{1}{990 \text{ ohm}} \times 0.7758 \text{ cm}^{-1} \\ &= \mathbf{0.000784 \text{ ohm}^{-1} \text{ cm}^{-1}} \end{aligned}$$

(iii) To calculate molar conductance of CaCl_2 **Formula used**

$$\text{Molar conductance, } \mu = \frac{\kappa \times 1000}{M}$$

Quantities given

$$\kappa = 0.000784 \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$M = \frac{22 \text{ g}}{111 \text{ g mol}^{-1}} = 0.198 \text{ mol}$$

Substitution of values

$$\begin{aligned} \mu &= \frac{0.000784 \text{ ohm}^{-1} \text{ cm}^{-1} \times 1000 \text{ cm}^3}{0.198 \text{ mol}} \\ &= \mathbf{3.95 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}} \end{aligned}$$

SOLVED PROBLEM 12. From the following data calculate the equivalent conductance (Λ_0) for NH_4OH

$$\text{Ba(OH)}_2 ; \Lambda_0 = 228.3 \text{ mhos}$$

$$\text{BaCl}_2 ; \Lambda_0 = 120.3 \text{ mhos}$$

$$\text{NH}_4\text{Cl} ; \Lambda_0 = 129.8 \text{ mhos}$$

SOLUTION :**Formula used**

$$\Lambda_0(\text{NH}_4\text{OH}) = \Lambda_0(\text{Ba(OH)}_2) + 2 \times \Lambda_0(\text{NH}_4\text{Cl}) - \Lambda_0(\text{BaCl}_2)$$

Quantities given

$$\Lambda_0[\text{Ba(OH)}_2] = 228.3 \text{ mhos}$$

$$\Lambda_0(\text{NH}_4\text{Cl}) = 129.8 \text{ mhos}$$

$$\Lambda_0(\text{BaCl}_2) = 120.3 \text{ mhos}$$

Substituting of values

$$\begin{aligned} \Lambda_0(\text{NH}_4\text{OH}) &= 228.3 + 2 \times 129.8 - 120.3 \\ &= 488.4 - 120.3 \\ &= \mathbf{367.4 \text{ mhos}} \end{aligned}$$

SOLVED PROBLEM 13. The resistance of a N/100 Solution of an electrolyte was found to be 210 ohm at 25 °C. Calculate the equivalent conductance of the solution at 25 °C. (Cell constant = 0.88)**SOLUTION : (i) To calculate the specific conductance****Formula used**

$$\kappa = \frac{1}{R} \times \text{Cell constant}$$

Quantities given

$$R = 210 \text{ ohm}$$

$$\text{cell constant} = 0.88 \text{ cm}^{-1}$$

Substitution of values

$$\begin{aligned}\kappa &= \frac{1}{210 \text{ ohm}} \times 0.88 \text{ cm}^{-1} \\ &= 0.004190 \text{ ohm}^{-1} \text{ cm}^{-1}\end{aligned}$$

(ii) To calculate the equivalent conductance**Formula used**

$$\text{Equivalent conductance} = \frac{\kappa \times 1000}{N}$$

Quantities given

$$\kappa = 0.004190 \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$N = \frac{1}{100} \text{ eqvt} = 0.01 \text{ eqvt}$$

Substitution of values

$$\begin{aligned}\text{Equivalent conductance} &= \frac{0.004190 \text{ ohm}^{-1} \text{ cm}^{-1} \times 1000 \text{ cm}^3}{0.01 \text{ eqvt}} \\ &= 419 \text{ ohm}^{-1} \text{ cm}^2 \text{ eqvt}^{-2}\end{aligned}$$

SOLVED PROBLEM 14. A conductance cell had a resistance of 165 ohms when filled with 0.02 molar KCl solution at 25 °C. For such solution specific conductance is 0.00277 mho cm⁻¹. The same cell filled with 0.01 molar NaCl had a resistance of 384 ohms. Calculate specific conductance and equivalent conductance of solution.

SOLUTION : (i) To calculate the cell constant.**Formula used**

$$\text{Cell constant} = \frac{\text{Specific conductance}}{\text{Observed conductance}}$$

Quantities given

$$\text{Specific conductance} = 0.00277 \text{ mho cm}^{-1}$$

$$\text{Observed conductance} = \frac{1}{R} = \frac{1}{165 \text{ ohm}} = 0.006061 \text{ ohm}^{-1}$$

Substitution of values

$$\text{Cell constant} = \frac{0.00277 \text{ mho cm}^{-1}}{0.006061 \text{ ohm}^{-1}} = 0.4570 \text{ cm}^{-1}$$

(ii) To calculate the specific conductance of NaCl solution**Formula used**

$$\kappa = \frac{1}{R} \times \text{cell constant}$$

Quantities given

$$R = 384 \text{ ohms}$$

$$\text{cell constant} = 0.4570 \text{ cm}^{-1}$$

Substitution of values

$$\begin{aligned}\kappa &= \frac{1}{384 \text{ ohm}} \times 0.4570 \text{ cm}^{-1} \\ &= 0.001190 \text{ ohm}^{-1} \text{ cm}^{-1} \\ &= 1.190 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}\end{aligned}$$

(iii) To calculate the equivalent conductance of 0.01M NaCl solution**Formula used**

$$\text{Equivalent conductance} = \frac{\text{Specific conductance} \times 1000}{N}$$

Quantities given

$$\text{Specific conductance} = 1.190 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$N = 0.01 \text{ M} = 0.01 \text{ eqvt}$$

Substitution of values

$$\begin{aligned}\text{Equivalent conductance} &= \frac{1.190 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1} \times 1000 \text{ cm}^3}{0.01 \text{ eqvt}} \\ &= \mathbf{119 \text{ ohm}^{-1} \text{ cm}^2 \text{ eqvt}^{-1}}\end{aligned}$$

SOLVED PROBLEM 15. The conductance of N/10 AgNO₃ solution taken in a cell with cell constant 0.9555 cm⁻¹ is 0.0099 ohm⁻¹. Calculate (i) specific conductance (ii) equivalent conductance

SOLUTION : (i) To calculate specific conductance**Formula used**

$$\kappa = \frac{1}{R} \times \text{Cell constant}$$

Quantities given

$$\frac{1}{R} = 0.0099 \text{ ohm}^{-1} \qquad \text{cell constant} = 0.9555 \text{ cm}^{-1}$$

Substitution of values

$$\begin{aligned}\kappa &= 0.0099 \text{ ohm}^{-1} \times 0.9555 \text{ cm}^{-1} \\ &= \mathbf{0.00946 \text{ ohm}^{-1} \text{ cm}^{-1}}\end{aligned}$$

(ii) To calculate equivalent conductance**Formula used**

$$\text{Equivalent conductance} = \frac{\text{Sp. conductance} \times 1000}{N}$$

Quantities given

$$\text{Sp. conductance} = 0.00946 \text{ ohm}^{-1} \text{ cm}^{-1} \qquad N = 1/10 = 0.1 \text{ eqvt}$$

Substitution of values

$$\begin{aligned}\text{Equivalent conductance} &= \frac{0.00946 \text{ ohm}^{-1} \text{ cm}^{-1} \times 1000 \text{ cm}^3}{0.1 \text{ eqvt}} \\ &= \mathbf{94.6 \text{ ohm}^{-1} \text{ cm}^2 \text{ eqvt}^{-1}}\end{aligned}$$

SOLVED PROBLEM 16. The resistance of a cell containing 0.02 M KCl was found to be 175 ohms. The specific conductance of this solution is $27.7 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25 °C. An exactly 0.1M solution of another substance in the same cell had a resistance of 579 ohms. Calculate the equivalent conductance of this substance.

SOLUTION : (i) To calculate the cell constant**Formula used**

$$\text{Cell constant} = \frac{\text{Specific conductance}}{\text{Observed conductance}}$$

Quantities given

$$\begin{aligned}\text{Specific conductance} &= 27.7 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1} \\ \text{Observed conductance} &= \frac{1}{R} = \frac{1}{175 \text{ ohm}} = 0.005714 \text{ ohm}^{-1}\end{aligned}$$

Substitution of values

$$\text{Cell constant} = \frac{27.7 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}}{0.005714 \text{ ohm}^{-1}} = 0.4847 \text{ cm}^{-1}$$

(ii) To calculate the specific conductance of the substance**Formula used**

$$\kappa = \frac{1}{R} \times \text{Cell constant}$$

Quantities given

$$R = 579 \text{ ohms}$$

$$\text{cell constant} = 0.4847 \text{ cm}^{-1}$$

Substitution of values

$$\kappa = \frac{0.4847 \text{ cm}^{-1}}{579 \text{ ohm}} = 0.000837 \text{ ohm}^{-1} \text{ cm}^{-1}$$

(iii) To calculate the equivalent conductance of the substance**Formula used**

$$\text{Equivalent conductance} = \frac{\kappa \times 1000}{N}$$

Quantities given

$$\kappa = 0.000837 \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$N = 0.01 \text{ eqvt}$$

Substitution of values

$$\begin{aligned} \text{Equivalent conductance} &= \frac{0.000837 \times 1000 \text{ cm}^3}{0.01 \text{ eqvt}} \\ &= 83.7 \text{ ohm}^{-1} \text{ cm}^{-2} \text{ eqvt}^{-1} \end{aligned}$$

SOLVED PROBLEM 17. The specific conductance of N/50 KCl solution is $0.002765 \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25°C . If the resistance of the solution contained in the cell is 1000 ohms, calculate the cell constant.

SOLUTION :**Formula used**

$$\text{Cell constant} = \frac{\text{Specific conductance}}{\text{Observed conductance}}$$

Quantities given

$$\text{Specific conductance} = 0.002765 \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$\text{Observed conductance} = \frac{1}{R} = \frac{1}{1000 \text{ ohm}} = 0.001 \text{ ohm}^{-1}$$

Substitution of values

$$\begin{aligned} \text{Cell constant} &= \frac{0.002765 \text{ ohm}^{-1} \text{ cm}^{-1}}{0.001 \text{ ohm}^{-1}} \\ &= 0.2765 \text{ cm}^{-1} \end{aligned}$$

SOLVED PROBLEM 18. Find specific conductivity of the solution if 0.5 M solution of a salt occupying a volume between two Pt electrodes 1.72 cm apart and of area 4.5 sq cm has a resistance of 15 ohms.

SOLUTION :**Formula used**

$$\kappa = \frac{1}{R} \times \frac{l}{a}$$

Quantities given

$$R = 15 \text{ ohm}$$

$$l = 1.72 \text{ cm}$$

$$a = 4.5 \text{ cm}^2$$

Substitution of values

$$\begin{aligned} \kappa &= \frac{1}{15 \text{ ohm}} \times \frac{1.72 \text{ cm}}{4.5 \text{ cm}^2} \\ &= 0.02548 \text{ ohm}^{-1} \text{ cm}^{-1} \end{aligned}$$

SOLVED PROBLEM 19. What will be the degree of ionisation of N/1000 acetic acid solution if its equivalent conductivity is 50 mhos and the value of equivalent conductivity at infinite dilution is 350 mhos ?

SOLUTION :**Formula used**

$$\alpha = \frac{\Lambda}{\Lambda_0}$$

Quantities given

$$\Lambda_0 = 350 \text{ mhos}$$

$$\Lambda = 50 \text{ mhos}$$

Substitution of values

$$\alpha = \frac{50 \text{ mhos}}{350 \text{ mhos}} = 0.142857$$

SOLVED PROBLEM 20. Resistance of 0.01 M aqueous solution of an electrolyte at room temperature is 420 ohm and cell constant is 0.84 cm⁻¹. Calculate the molar conductance.

SOLUTION : (i) To calculate the specific conductance**Formula used**

$$\kappa = \frac{l}{R} \times \text{Cell constant}$$

Quantities given

$$R = 420 \text{ ohm}^{-1}$$

$$\text{cell constant} = 0.84 \text{ cm}^{-1}$$

Substitution of values

$$\begin{aligned} \kappa &= \frac{1}{420 \text{ ohm}^{-1}} \times 0.84 \text{ cm}^{-1} \\ &= 0.002 \text{ ohm cm}^{-1} \end{aligned}$$

(ii) To calculate the molar conductance**Formula used**

$$\text{Molar conductance, } \mu = \frac{\text{Specific conductance} \times 1000}{\text{Molarity}}$$

Quantities given

$$\text{Specific conductance} = 0.002 \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$\text{Molarity} = 0.01 \text{ M}$$

Substitution of values

$$\begin{aligned} \mu &= \frac{0.002 \text{ ohm}^{-1} \text{ cm}^{-1} \times 1000 \text{ cm}^3}{0.01 \text{ M}} \\ &= 200 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1} \end{aligned}$$

SOLVED PROBLEM 21. The equivalent conductance at infinite dilution (Λ_0) of HCl, CH₃COONa and NaCl are 426.16, 91.0 and 126.45 ohm⁻¹cm²g eqvt⁻¹ respectively. Calculate Λ_0 of acetic acid.

SOLUTION :**Formula used**

$$\Lambda_0(\text{CH}_3\text{COOH}) = \Lambda_0(\text{CH}_3\text{COONa}) + \Lambda_0(\text{HCl}) - \Lambda_0(\text{NaCl})$$

Quantities given

$$\Lambda_0(\text{CH}_3\text{COONa}) = 91.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ g eqvt}^{-1}$$

$$\Lambda_0(\text{HCl}) = 426.16 \text{ ohm}^{-1} \text{ cm}^2 \text{ g eqvt}^{-1}$$

$$\Lambda_0(\text{NaCl}) = 126.45 \text{ ohm}^{-1} \text{ cm}^2 \text{ g eqvt}^{-1}$$

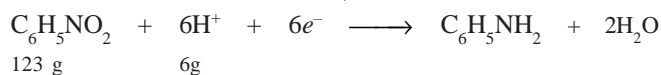
Substitution of values

$$\begin{aligned} \Lambda_0(\text{CH}_3\text{COOH}) &= 91.0 + 426.16 - 126.45 \text{ ohm}^{-1} \text{ cm}^2 \text{ g eqvt}^{-1} \\ &= 390.71 \text{ ohm}^{-1} \text{ cm}^2 \text{ g eqvt}^{-1} \end{aligned}$$

SOLVED PROBLEM 22. Calculate the quantity of electricity that would be required to reduce 12.3 g nitrobenzene to aniline, if the current efficiency for the process is 50%. If the potential drop across the cell is 3.0 volts, how much energy will be consumed ?

SOLUTION : (i) To calculate the quantity of electricity

The reaction is



Hydrogen required for the reduction of 123 g of $\text{C}_6\text{H}_5\text{NO}_2 = 6 \text{ g}$

and Hydrogen required for the reduction of 12.3 g of $\text{C}_6\text{H}_5\text{NO}_2 = \frac{6 \text{ g} \times 12.3 \text{ g}}{123 \text{ g}} = 0.6 \text{ g}$

1 g of Hydrogen \equiv 96500 coulombs

$$\begin{aligned} \therefore 0.6 \text{ g of Hydrogen} &= \frac{96500 \text{ coulomb} \times 0.6 \text{ g}}{1.0 \text{ g}} \\ &= 57900 \text{ coulombs} \end{aligned}$$

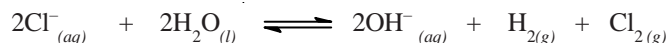
The quantity of electricity required for the reaction

$$\begin{aligned} &= \frac{57900 \text{ coulomb} \times 100}{50} \quad [\because \text{current efficiency} = 50\%] \\ &= \mathbf{115800 \text{ coulombs}} \end{aligned}$$

(ii) To calculate the energy consumed

$$\begin{aligned} \text{Total energy consumed} &= 3 \text{ volts} \times 115800 \text{ coulombs} \\ &= 347400 \text{ J} \quad [\because \text{volt} \times \text{coulomb} = \text{J}] \\ &= \mathbf{347.4 \text{ kJ}} \end{aligned}$$

SOLVED PROBLEM 23. An aqueous solution of NaCl on electrolysis gives $\text{H}_2(g)$, $\text{Cl}_2(g)$ and $\text{NaOH}_{(aq)}$ according to the reaction.



A direct current of 25 amperes with a current efficiency of 62% is passed through 20% litres of NaCl solution (20% by weight). How long will it take to produce 1 Kg of Cl_2 ? What will be the molarity of solution with respect to hydroxide ion ? (Assuming no loss due to evaporation).

SOLUTION : (i) To calculate time to produce 1 kg of Cl_2

Formula used

$$m = Z \times I \times t \quad \text{where } Z = \frac{E}{96500}$$

or

$$m = \frac{E}{96500} \times I \times t$$

Quantities given

$$m = 1000 \text{ g}$$

$$E = 35.5 \text{ g} \quad I = \frac{25 \text{ amp} \times 62}{100} = 15.5 \text{ amp}$$

Substitution of values

$$1000 \text{ g} = \frac{35.5 \text{ g}}{96500} \times 15.5 \times t$$

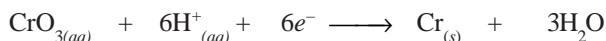
or

$$\begin{aligned} t &= \frac{1000 \times 96500}{35.5 \times 15.5} \text{ sec} \\ &= 175374 \text{ sec} \\ &= \mathbf{48.71 \text{ hrs}} \end{aligned}$$

(ii) To calculate the molarity of solution with respect to OH^- ions.

$$\begin{aligned}\text{No of moles of } \text{Cl}_2 \text{ produced} &= \frac{100\text{g}}{71 \text{ g mol}^{-1}} = 1.4085 \text{ moles} \\ \text{Amount of } \text{OH}^- \text{ released during the reaction} &= 2 \times 1.4085 \text{ moles} \\ &= 2.817 \text{ moles} \quad [\because \text{Cl}_2 \equiv 2\text{OH}^-] \\ \text{Molarity of solution w.r.t. } \text{OH}^- \text{ ions} &= \frac{2.817 \text{ moles}}{20 \text{ litres}} \\ &= \mathbf{0.14085 \text{ M}}\end{aligned}$$

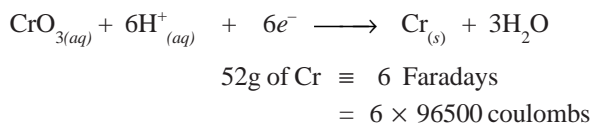
SOLVED PROBLEM 24. Chromium metal can be plated out from an acidic solution containing CrO_3 according to the following equation :



Calculate (i) how many grams of chromium will be plated out by 24,000 coulombs and (ii) how long will it take to plate out 1.5 g of chromium by using 12.5 ampere current ?

SOLUTION : (ii) To calculate the amount of chromium that will be plated out

The reaction is



Thus 6×96500 coulomb of electricity produce Cr = 52g

$$1 \text{ coulomb of electricity produce Cr} = \frac{52 \text{ g}}{6 \times 96500 \text{ coulomb}}$$

$$\begin{aligned}24000 \text{ coulombs of electricity produce Cr} &= \frac{52 \times 24000 \text{ coulomb}}{6 \times 96500 \text{ coulomb}} \\ &= \mathbf{2.15544 \text{ g}}\end{aligned}$$

(ii) To calculate the time to plate out 1.5 g of chromium by using 12.5 ampere current

Formula used

$$m = Z \times I \times t$$

where

$$Z = \frac{52}{6 \times 96500} \quad [\because \text{Eq wt of Cr} = 52]$$

Quantities given

$$m = 1.5 \text{ g}$$

$$Z = \frac{52}{6 \times 96500} \text{ g} \quad I = 12.5 \text{ amp.}$$

Substitution of values

$$1.5 \text{ g} = \frac{52 \text{ g} \times 12.5 \text{ amp} \times t}{6 \times 96500}$$

or

$$\begin{aligned}t &= \frac{1.5 \times 6 \times 96500}{52 \times 12.5} \\ &= \mathbf{1336.15 \text{ sec}}\end{aligned}$$

SOLVED PROBLEM 25. An electric current of 2.0 ampere was passed through acidulated water for two hours. Calculate the volumes of hydrogen gas produced at STP. The electrochemical equivalent of hydrogen is 1×10^{-5} g.

SOLUTION : (i) To calculate the amount of H_2 liberated**Formula used**

$$m = Z \times I \times t$$

Quantities given

$$Z = 1 \times 10^{-5} \text{ g}$$

$$I = 2.0 \text{ ampere}$$

$$t = 2 \times 60 \times 60 \text{ sec}$$

Substitution of values

$$\begin{aligned} m &= 1 \times 10^{-5} \times 2.0 \times 7200 \text{ g} \\ &= 0.144 \text{ g} \end{aligned}$$

(ii) To calculate the volume of hydrogen gas at STP

$$1 \text{ mol of } H_2 = 22.4 \text{ litre at STP}$$

$$2 \text{ g of } H_2 = 22.4 \text{ litre at STP}$$

$$\begin{aligned} 0.144 \text{ g of } H_2 &= \frac{22.4 \text{ lit} \times 0.144 \text{ g}}{2 \text{ g}} \\ &= \mathbf{1.612 \text{ lit}} \end{aligned}$$

SOLVED PROBLEM 26. What current strength in ampere will be required to deposit 100 of silver from $AgNO_3$ solution in one hour ?

SOLUTION :**Formula used**

$$m = Z \times I \times t$$

Quantities given

$$t = 3600 \text{ sec}$$

$$m = 100 \text{ g}$$

$$Z = \frac{108 \text{ g}}{96500 \text{ C}}$$

Substitution of values

$$100 \text{ g} = \frac{108 \text{ g}}{96500 \text{ C}} \times I \times 3600 \text{ sec}$$

or

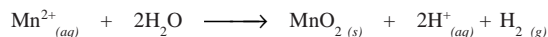
$$\begin{aligned} I &= \frac{100 \times 96500}{108 \times 3600} \text{ ampere} \\ &= \mathbf{24.82 \text{ ampere}} \end{aligned}$$

ADDITIONAL PRACTICE PROBLEMS

- How many atoms of copper will be deposited from a solution of $CuSO_4 \cdot 5H_2O$ by a current of 25 milliamperes for 100 sec ?
Answer. 7.797×10^{18} atoms of Cu
- A current of 2.0 ampere is passed through 500 ml of 0.1 M solution of $ZnSO_4$ for 4 minutes with a current efficiency of 90%. Find out the molarity of Zn^{2+} after deposition of Zn assuming volume remain constant.
Answer. 0.0977 M
- Calculate the quantity of electricity that will be required to produce 355 g chlorine gas by the electrolysis of a concentrated solution of NaCl. Also calculate the volume of hydrogen gas liberated at 27 °C and 1 atm pressure during the process.
Answer. 10 F ; 123.07 lit

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4. A current 4.0 amperes is passed for 8 hours between nickel electrodes in 500 ml of 2M solution of nickel nitrate. What will be the molarity of the solution at the end of electrolysis ?
Answer. 0.806 M
5. A solution of copper sulphate weighing 20g was electrolysed using 0.02 Faraday of electricity. Calculate the weight of the resulting solution.
Answer. 9.205 g
6. A current deposits 10 g of copper in 30 hours from a solution of Cu^{2+} ions. Calculate the strength of the current in amperes.
Answer. 0.2814 amp
7. How many grams of iodine are produced when a current of 8.52 mA flows through an aqueous solution of potassium iodide using platinum electrodes for 10 minutes ?
Answer. 0.00673 g
8. When molten lithium chloride, LiCl , is electrolysed, lithium metal is liberated at the cathode. How many grams of lithium are liberated when 5000C of charge passes through the cell ?
Answer. 0.360 g
9. A potential difference of 10 volts is applied to the ends of a column of 0.1 N AgNO_3 solution, 2 cm in diameter and 6 cm in length gives a current of 0.99 ampere. Calculate the specific conductance and equivalent conductance of the solution.
Answer. $0.18917 \text{ ohm}^{-1}\text{cm}^{-1}$; $1891.7 \text{ ohm}^{-1}\text{cm}^{-2}\text{eqvt}^{-1}$
10. Specific conductance of 0.1 N solution of an electrolyte is $0.02 \text{ ohm}^{-1}\text{cm}^{-1}$. Calculate its equivalent conductance.
Answer. $200 \text{ ohm}^{-1}\text{cm}^2\text{eqvt}^{-1}$
11. Specific conductance of 0.02 N KCl at 298 K is $0.002768 \text{ ohm}^{-1}$ and it has resistance of 500 ohms. An 0.25 N solution of another salt kept in the same cell was found to have resistance of 300 ohms at 298 K. Calculate the cell constant and equivalent conductance of the salt solution.
Answer. 1.384; $18.45 \text{ ohm}^{-1}\text{cm}^2\text{eqvt}^{-1}$
12. Electrolysis of a solution of MnSO_4 in aqueous sulphuric acid is a method for the preparation of MnO_2 as per reaction :



Passing a current of 27 A for 24 hours gives one kg of MnO_2 . What is the value of current efficiency.

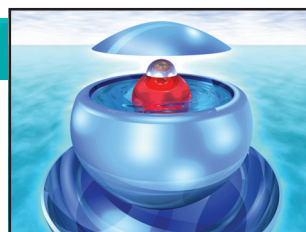
Answer. 95.2%

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Theory of Electrolytic Dissociation

CHAPTER

KEY CONCEPTS AND EQUATIONS



ARRHENIUS THEORY OF IONISATION

According to this theory an electrolyte on dissolution in water splits up into ions which reunite to form neutral molecules and there is a state of equilibrium between the undissociated molecules and the ions.

$$K = \frac{[A^+][B^-]}{[AB]}$$

where K is called the Dissociation constant.

TRANSPORT NUMBER AND ITS DETERMINATION

The fraction of the total current carried by the cation or the anion is called Transport number. It is given by

$$t_+ = \frac{v_+}{v_+ + v_-} \quad \text{and} \quad t_- = \frac{v_-}{v_+ + v_-}$$

HITTORF'S METHOD

It is based on Hittorf's rule – the loss of concentration around any electrode is proportional to the speed of the ion moving away from that electrode.

(i) When electrodes are unattackable

$$\begin{aligned} \text{Transport number of } Ag^+ &= \frac{\text{Fall in concentration around anode in g eqvt}}{\text{Amt. of Ag deposited in g eqvt}} \\ &= \frac{d}{W} \end{aligned}$$

(ii) When electrodes are attackable

$$\text{Transport number of } Ag^+ = \frac{W - e}{W}$$

where W is the increase in concentration of Ag^+ ions if no Ag^+ ions had migrated from the anode and e is the increase in concentration of anodic solution.

MOVING BOUNDARY METHOD

It is based on the direct observation of migration of ions under the influence of applied potential.

$$t_{A^+} = \frac{s \times l \times c}{n}$$

where l is distance through which the boundary moves, s the area of cross-section of the tube, $n = Q/F$, Q being the quantity of current passed and F stands for Faraday and c is original concentration of A^+ ions.

KOHLRAUSCH'S LAW

It states that the equivalent conductance of an electrolyte at infinite dilution is equal to the sum of the equivalent conductances of the component ions.

$$\lambda = \lambda_a + \lambda_c$$

where λ_a is the equivalent conductance of the anion and λ_c that of the cations.

ABSOLUTE IONIC MOBILITIES

The absolute ionic mobility of an ion is the velocity of an ion in centimeters per second under a potential gradient of one volt per centimeter. It has been found that the ionic conductance is directly proportional to the ionic mobility *i.e.*

$$\lambda_a = k U_a \quad \text{and} \quad \lambda_c = k U_c$$

where K is the constant of proportionality.

DEGREE OF DISSOCIATION

The degree of dissociation, α , of an electrolyte at the dilution V is given by

$$\alpha = \frac{\lambda_v}{\lambda_\infty}$$

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. A solution containing 0.00739 g of $AgNO_3$ per gram of water was electrolysed between silver electrodes. During the experiment 0.0078 g of silver was deposited in a silver coulometer placed in series. At the end of experiment, the anodic solution contained 23.14 g of water and 0.236 g of $AgNO_3$. What are the transport numbers of Ag^+ and NO_3^- ions?

SOLUTION : (i) To calculate the transport number of Ag^+

Before Electrolysis :

Mass of water = 1 g

Mass of $AgNO_3$ = 0.00739 g

$$\begin{aligned} \text{No. of gram eqvt. of Ag} &= \frac{0.00739}{170} \\ &= 4.347 \times 10^{-5} \end{aligned}$$

After Electrolysis

Mass of water = 23.14 g

Mass of $AgNO_3$ = 0.236 g

$$\begin{aligned} \text{No. of g equivalents of Ag in 1 g of water} &= \frac{0.236}{23.14} \times \frac{1}{170} \\ &= 5.992 \times 10^{-5} \end{aligned}$$

Increase in concentration of Ag^+ in the anodic compartment when no silver ions migrate

$$\begin{aligned} &= \frac{0.0078}{170} \\ &= 4.588 \times 10^{-5} \end{aligned}$$

Increase in concentration of Ag^+ ions in the anodic compartment when Ag^+ ions migrate

$$\begin{aligned} &= \text{Conc. of Ag after electrolysis} - \text{Conc. of Ag before electrolysis} \\ &= 5.992 \times 10^{-5} - 4.347 \times 10^{-5} \\ &= 1.645 \times 10^{-5} \end{aligned}$$

$$\begin{aligned} \text{Fall in conc. of } Ag^+ \text{ in anodic compartment} &= 4.588 \times 10^{-5} - 1.645 \times 10^{-5} \\ &= 2.943 \times 10^{-5} \end{aligned}$$

$$\begin{aligned}
 \text{Transport number of Ag}^+ \text{ ions} &= \frac{\text{Fall in conc. around anode}}{\text{Silver deposited on Ag electrode}} \\
 &= \frac{2.943 \times 10^{-5}}{4.588 \times 10^{-5}} \\
 &= \mathbf{0.641}
 \end{aligned}$$

(ii) To calculate the transport number of NO_3^- ions

$$\begin{aligned}
 &= 1 - t_{\text{Ag}^+} \\
 &= 1 - 0.641 \\
 &= \mathbf{0.359}
 \end{aligned}$$

SOLVED PROBLEM 2. The specific conductivity of saturated solution of silver chloride at 18°C is 1.24×10^{-6} mhos after subtracting that of water. The mobilities of Ag^+ and Cl^- ions at this temperature are 53.8 and 65.3 respectively. Calculate the solubility of silver chloride in grams per litre.

SOLUTION : (i) To calculate the volume of solution that contain 1 g equivalent of AgCl.

Formula used

$$\lambda = \kappa \times V$$

Quantities given

$$\kappa = 1.24 \times 10^{-6} \text{ mhos}$$

$$\lambda = \lambda_{\text{Ag}^+} + \lambda_{\text{Cl}^-} = 53.8 + 65.3 = 119.1$$

Substitution of values

$$119.1 = 1.24 \times 10^{-6} \times V$$

or

$$\begin{aligned}
 V &= \frac{119.1}{1.24 \times 10^{-6}} \\
 &= 9.6048 \times 10^7 \text{ ml}
 \end{aligned}$$

(ii) To calculate the solubility of AgCl in gram per litre

$$9.6048 \times 10^7 \text{ ml contain AgCl} = 1 \text{ g eqvt} = 143.5 \text{ g}$$

$$\begin{aligned}
 1000 \text{ ml contain AgCl} &= \frac{143.5 \times 1000}{9.604 \times 10^7} \\
 &= \mathbf{1.494 \times 10^{-3}}
 \end{aligned}$$

SOLVED PROBLEM 3. In a moving boundary experiment 0.01 N HCl solution was floated on a lithium chloride solution. The tube used had a diameter of 1 cm. When a current of 11.0 milliampere was passed for 20 minutes, the H^+ ions – Li^+ ions boundary moved through 13.9 cm. Calculate the transport numbers of H^+ and Cl^- ions in HCl solution used.

SOLUTION : (i) To calculate the transport no. of H^+

Formula used

$$t_{\text{H}^+} = \frac{s \times l \times F \times c}{Q}$$

Quantities given

$$s = \pi r^2 = \frac{22}{7} \times 0.5 \times 0.5$$

$$l = 13.9 \text{ cm}$$

$$F = 96500 \text{ coulomb}$$

$$c = 0.01 \text{ N}$$

$$Q = 11 \times 10^{-3} \times 20 \times 60$$

Substitution of values

$$\begin{aligned}
 t_{\text{H}^+} &= \frac{22}{7} \times \frac{0.5 \times 0.5 \times 13.9 \times 96500 \times 0.01}{11 \times 10^{-3} \times 20 \times 60} \\
 &= \mathbf{0.7984}
 \end{aligned}$$

(ii) To calculate the transport no. of Cl^- .**Formula used**

$$t_{\text{Cl}^-} = 1 - t_{\text{H}^+}$$

Quantities given

$$t_{\text{H}^+} = 0.7984$$

Substitution of values

$$\begin{aligned} t_{\text{Cl}^-} &= 1 - 0.7984 \\ &= \mathbf{0.2016} \end{aligned}$$

SOLVED PROBLEM 4. Calculate the equivalent conductivity at 20 °C of NH_4OH at infinite dilution.Given: $\lambda_o(\text{NH}_4\text{Cl}) = 130$, $\lambda_o(\text{OH}^-) = 174$ and $\lambda_o(\text{Cl}^-) = 66$.**SOLUTION :****Formula used**

$$\lambda_o(\text{NH}_4\text{OH}) = \lambda_o(\text{NH}_4\text{Cl}) + \lambda_o(\text{OH}^-) - \lambda_o(\text{Cl}^-)$$

Quantities given

$$\lambda_o(\text{NH}_4\text{Cl}) = 130$$

$$\lambda_o(\text{OH}^-) = 174$$

$$\lambda_o(\text{Cl}^-) = 66$$

Substitution of values

$$\begin{aligned} \lambda_o(\text{NH}_4\text{OH}) &= 130 + 174 - 66 \\ &= \mathbf{238} \end{aligned}$$

SOLVED PROBLEM 5. The absolute velocity of Ag^+ is $0.00057 \text{ cm sec}^{-1}$ and that of NO_3^- is $0.00069 \text{ cm sec}^{-1}$. Assuming complete dissociation, calculate the specific conductivity of 0.01 M solution of silver nitrate.**SOLUTION :****Formula used**

$$\kappa V = \lambda_{\infty} = \lambda_{\text{Ag}^+} + \lambda_{\text{NO}_3^-}$$

Quantities given

$$\lambda_{\text{Ag}^+} = 0.00057 \times 96500$$

$$\lambda_{\text{NO}_3^-} = 0.00069 \times 96500$$

$$V = \frac{1000}{0.01}$$

Substitution of values

$$\begin{aligned} \kappa &= \frac{96500(0.00057 + 0.00069) \times 0.01}{1000} \text{ mhos} \\ &= \mathbf{0.00121 \text{ mhos}} \end{aligned}$$

SOLVED PROBLEM 6. The speed ratio of silver and nitrate ions in AgNO_3 electrolysed between silver electrodes was found to be 0.89. Calculate the transference number of silver and nitrate ions.**SOLUTION : (i) To calculate the transference no. of NO_3^- ions.****Formula used**

$$t_- = \frac{1}{1 + r}$$

Quantities given

$$r = 0.89$$

Substitution of values

$$t_- = \frac{1}{1 + 0.89} = \frac{1}{1.89} = \mathbf{0.5291}$$

(ii) To calculate the transference number of Ag^+ ions.

Formula used

$$\begin{aligned} t_{\text{Ag}^+} &= 1 - t_{\text{NO}_3^-} \\ &= 1 - 0.5291 \\ &= \mathbf{0.4709} \end{aligned}$$

SOLVED PROBLEM 7. In a moving boundary experiment with 0.1 N KCl using 0.65 N LiCl as indicator solution, a constant current of 0.006 amp was passed for 1900 secs and the boundary was observed to move through 5 cm in a tube of 0.1142 cm^2 cross-section. Calculate the transport number of K^+ and Cl^- ions.

SOLUTION : (i) To calculate the transport number of K^+ ions.

Formula used

$$t_{\text{K}^+} = \frac{s \times l \times F \times c}{Q}$$

Quantities given

$$s = 0.1142 \text{ cm}^2$$

$$l = 5 \text{ cm}$$

$$F = 96500 \text{ coulomb}$$

$$c = 0.1$$

$$Q = 0.006 \times 1900 \text{ coulomb}$$

Substitution of values

$$\begin{aligned} t_{\text{K}^+} &= \frac{0.1142 \times 5 \times 96500 \times 0.1}{1000 \times 0.006 \times 1900} \\ &= \mathbf{0.4833} \end{aligned}$$

(ii) To calculate the transport number of Cl^- ions

Formula used

$$t_{\text{Cl}^-} = 1 - t_{\text{K}^+}$$

Quantities given

$$t_{\text{K}^+} = 0.4833$$

Substitution of values

$$\begin{aligned} t_{\text{Cl}^-} &= 1 - 0.4833 \\ &= \mathbf{0.5167} \end{aligned}$$

SOLVED PROBLEM 8. A dilute solution of silver nitrate was electrolysed using platinum electrodes. After passing small current for three hours, a fall of 0.00064 g equivalent of electrolyte occurred in the anionic solution. The weight of copper deposited was found to be 0.05088 gm. Calculate the transport number of silver ions.

SOLUTION :

Formula used

$$\text{Transport No. of } \text{Ag}^+ \text{ ions} = \frac{\text{Fall in concentration}}{\text{Amt. of Cu deposited in g eqvt}}$$

Quantities given

$$\text{Fall in Concentration} = 0.00064 \text{ g eqvt.}$$

$$\text{Amt. of Cu deposited in g eqvt} = \frac{0.05088}{31.5}$$

Substitution of values

$$\begin{aligned} \text{Transport No. of } \text{Ag}^+ \text{ ions} &= \frac{0.00064 \times 31.5}{0.05088} \\ &= \mathbf{0.40} \end{aligned}$$

SOLVED PROBLEM 9. A solution of AgNO_3 containing 0.5066 g of the salt in 60 g of solution was electrolysed between silver electrodes. After electrolysis 50 g of the anode solution found to contain 0.5186 g of AgNO_3 when a current of one ampere was passed for 118 seconds. Calculate the transport numbers of Ag^+ and NO_3^- ions.

SOLUTION : (i) To calculate the transport number of Ag^+ ions.

After electrolysis

Weight of anodic solution taken = 50 g

Weight of AgNO_3 present in it = 0.5186 g

Weight of water = 49.4814 g

Before Electrolysis

Weight of AgNO_3 solution = 60 g

Weight of AgNO_3 present = 0.5066 g

Weight of water = 59.4934 g

Weight of AgNO_3 present in 49.4814 g

$$\text{of water} = \frac{0.5066}{59.4934} \times 49.4814$$

$$= 0.421 \text{ g}$$

Observed increase in the weight of AgNO_3 in anodic compartment due to electrolysis

$$= 0.5186 - 0.421 \text{ g}$$

$$= 0.0976 \text{ g}$$

$$= \frac{0.0976}{170} \text{ g equiv of } \text{AgNO}_3$$

$$= 5.741 \times 10^{-4} \text{ g}$$

$$\text{Quantity of electricity passed} = I \times t$$

$$= 1 \text{ amp} \times 118 \text{ sec}$$

$$= 118 \text{ coulombs}$$

$$\begin{aligned} \text{Amount of } \text{AgNO}_3 \text{ liberated when 118 coulombs of electricity are passed} &= \frac{118}{96500} \\ &= 1.223 \times 10^{-3} \text{ g} \end{aligned}$$

Loss around the anode due to migration of ions

$$= 1.223 \times 10^{-3} - 5.741 \times 10^{-4}$$

$$= 6.489 \times 10^{-4}$$

$$\begin{aligned} \text{Transport number of } \text{Ag}^+ \text{ ions} &= \frac{6.489 \times 10^{-4}}{1.223 \times 10^{-3} \text{ g}} \\ &= \mathbf{0.530} \end{aligned}$$

(ii) To calculate the transport number of NO_3^- ions

$$\text{Transport number of } \text{NO}_3^- \text{ ions} = 1 - \text{transport number of } \text{Ag}^+$$

$$= 1 - 0.530$$

$$= \mathbf{0.470}$$

SOLVED PROBLEM 10. The equivalent conductance at infinite dilution (Λ_o) of HCl , CH_3COONa and NaCl are 426.16, 91.0 and 126.45 $\text{ohm}^{-1} \text{cm}^2 \text{g equiv}^{-1}$ respectively. Calculate Λ_o of acetic acid.

SOLUTION :

Formula used

$$\Lambda_o(\text{CH}_3\text{COOH}) = \Lambda_o(\text{CH}_3\text{COONa}) + \Lambda_o(\text{HCl}) - \Lambda_o(\text{NaCl})$$

Quantities given

$$\Lambda_o(\text{CH}_3\text{COONa}) = 91.0 \text{ ohm}^{-1} \text{cm}^2 \text{g equiv}^{-1}$$

$$\Lambda_o(\text{NaCl}) = 126.45 \text{ ohm}^{-1} \text{cm}^2 \text{g equiv}^{-1}$$

$$\Lambda_o(\text{HCl}) = 426.16 \text{ ohm}^{-1} \text{cm}^2 \text{g equiv}^{-1}$$

Substitution of values

$$\begin{aligned}\Lambda_o(\text{CH}_3\text{COOH}) &= 91.0 + 426.16 - 126.45 \text{ ohm}^{-1} \text{ cm}^2 \text{ g equiv}^{-1} \\ &= \mathbf{390.71 \text{ ohm}^{-1} \text{ cm}^2 \text{ g equiv}^{-1}}\end{aligned}$$

SOLVED PROBLEM 11. The specific conductance of a saturated solution of AgCl is $1.55 \times 10^{-6} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 25°C . The ion conductance of Ag^+ and Cl^- are 61.94 and 76.34 $\text{ohm}^{-1} \text{ cm}^2$ respectively. Calculate the solubility of AgCl in gram equivalent per litre at 25°C . Neglect the specific conductance of water.

SOLUTION :**Formula used**

$$\mu = \frac{\kappa \times 1000}{s}$$

Quantities given

$$\mu = \mu_{\text{Ag}^+} + \mu_{\text{NO}_3^-} = 61.94 + 76.34 = 138.28 \text{ ohm}^{-1} \text{ cm}^2 \quad \kappa = 1.55 \times 10^{-6} \text{ ohm cm}^{-1}$$

Substitution of values

$$138.28 \text{ ohm}^{-1} \text{ cm}^{-1} = \frac{1.55 \times 10^{-6} \times 1000}{s}$$

or

$$\begin{aligned}s &= \frac{1.55 \times 10^{-6} \times 1000}{138.28} \\ &= \mathbf{1.1209 \times 10^{-5} \text{ mol lit}^{-1}}\end{aligned}$$

SOLVED PROBLEM 12. In a moving boundary experiment with 0.1 N KCl solution, the boundary moved 4.94 cm during 67 minutes when a current of 5.21 A was used. The cross-sectional area of the tube was 0.230 cm^2 . Calculate the transport number of K^+ ions.

SOLUTION :**Formula used**

$$t_{\text{K}^+} = \frac{s \times l \times F \times c}{Q}$$

Quantities given

$$s = 0.230 \text{ cm}^2$$

$$l = 4.94 \text{ cm}$$

$$F = 96500 \text{ coulomb}$$

$$c = 0.1 \text{ N}$$

$$Q = 5.21 \times 67 \times 60 \text{ coulombs}$$

Substitution of values

$$\begin{aligned}t_{\text{K}^+} &= \frac{0.230 \times 4.94 \times 96500 \times 0.1}{5.21 \times 67 \times 60} \\ &= \mathbf{0.523}\end{aligned}$$

SOLVED PROBLEM 13. Molar conductances of NaOH, NaCl and NH_4Cl are 248.61, 126.45 and $149.75 \text{ } \Omega^{-1} \text{ m}^2 \text{ mol}^{-1}$. Calculate the molar conductance of NH_4OH .

SOLUTION :**Formula used**

$$\mu_{(\text{NH}_4\text{OH})} = \mu_{(\text{NaOH})} + \mu_{(\text{NH}_4\text{Cl})} - \mu_{(\text{NaCl})}$$

Quantities given

$$\mu_{(\text{NaOH})} = 248.61 \text{ } \Omega^{-1} \text{ m}^2 \text{ mol}^{-1}$$

$$\mu_{(\text{NH}_4\text{Cl})} = 149.75 \text{ } \Omega^{-1} \text{ m}^2 \text{ mol}^{-1}$$

$$\mu_{(\text{NaCl})} = 126.45 \text{ } \Omega^{-1} \text{ m}^2 \text{ mol}^{-1}$$

Substitution of values

$$\begin{aligned}\mu_{(\text{NH}_4\text{OH})} &= 248.61 + 149.75 - 126.45 \text{ } \Omega^{-1} \text{ m}^2 \text{ mol}^{-1} \\ &= \mathbf{271.91 \text{ } \Omega^{-1} \text{ m}^2 \text{ mol}^{-1}}\end{aligned}$$

SOLVED PROBLEM 14. In a particular experiment on KCl the apparatus consisted of a tube of diameter 4.176 mm and it contained an aqueous solution of KCl at a concentration of 0.021 mol lit⁻¹. A steady current of 1.82 mA was passed and the cationic boundary advanced 3.18 mm in 100 sec. Find transport number of K⁺ and Cl⁻.

SOLUTION : (i) To calculate the transport number of K⁺

Formula used

$$t_{K^+} = \frac{s \times l \times F \times c}{Q}$$

Quantities given

$$s = \frac{22}{7} \times \frac{0.4176}{2} \times \frac{0.4176}{2} \text{ cm}^2$$

$$l = 3.18 \text{ mm} = 0.318 \text{ cm}$$

$$Q = 1.82 \times 10^{-3} \times 100 \text{ coulomb}$$

$$F = 96500 \text{ coulomb}$$

$$c = 0.021 \text{ mol lit}^{-1}$$

Substitution of values

$$\begin{aligned} t_{K^+} &= \frac{22}{7} \times \frac{0.4176}{2} \times \frac{0.4176}{2} \times \frac{0.318 \times 96500 \times 0.021}{1.82 \times 10^{-3} \times 100} \\ &= \mathbf{0.4847} \end{aligned}$$

(ii) To calculate the transport number of Cl⁻

Formula used

$$t_{Cl^-} = 1 - t_{K^+}$$

Quantities given

$$t_{K^+} = 0.4847$$

Substitution of values

$$\begin{aligned} t_{Cl^-} &= 1 - 0.4847 \\ &= \mathbf{0.5153} \end{aligned}$$

SOLVED PROBLEM 15. A 0.05 M NaOH solution offered a resistance of 31.6 ohm in a conductivity cell at 298 K. If the cell constant of the cell is 0.367 cm⁻¹ find out the molar conductivity of sodium hydroxide solution.

SOLUTION : (i) To calculate the specific conductivity of NaOH solution

Formula used

$$\text{Specific conductivity, } \kappa = \frac{\text{Cell constant}}{\text{Resistance}}$$

Quantities given

$$\text{Cell constant} = 0.367 \text{ cm}^{-1}$$

$$\text{Resistance} = 31.6 \text{ ohm}$$

Substitution of values

$$\begin{aligned} \text{Specific conductivity, } \kappa &= \frac{0.367 \text{ cm}^{-1}}{31.6 \text{ ohm}} \\ &= 0.0116 \text{ ohm}^{-1} \text{ cm}^{-1} \end{aligned}$$

(ii) To calculate the molar conductivity of NaOH solution

Formula used

$$\Lambda_m = \frac{1000 \times \kappa}{c}$$

Quantities given

$$\kappa = 0.0116 \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$c = 0.05 \text{ M}$$

Substitution of values

$$\begin{aligned} \Lambda_m &= \frac{1000 \times 0.0116 \text{ ohm}^{-1} \text{ cm}^{-1}}{0.05 \text{ M}} \\ &= 232.278 \text{ ohm}^{-1} \text{ cm}^{-1} \end{aligned}$$

SOLVED PROBLEM 16. The resistance of 0.1 M KCl solution in a conductance cell is 300 ohm and specific conductance of 0.1 M KCl is $1.29 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$. The resistance of a 0.1 M NaCl solution in the same cell is 380 ohm. Calculate the equivalent conductance of the 0.1 M NaCl solution.

SOLUTION : (i) To calculate the cell constant**Formula used**

$$\kappa = \frac{1}{R} \times \text{cell constant}$$

Quantities given

$$\kappa = 1.29 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$R = 300 \text{ ohm}$$

Substitution of values

$$\begin{aligned} 1.29 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1} &= \frac{1}{300 \text{ ohm}} \times \text{cell constant} \\ \text{cell constant} &= 300 \text{ ohm} \times 1.29 \times 10^{-2} \text{ ohm}^{-1} \text{ cm}^{-1} \\ &= 3.87 \text{ cm}^{-1} \end{aligned}$$

(ii) To calculate the equivalent conductance of 0.1 M NaCl solution**Formula used**

$$\Lambda = \kappa \times \frac{1000}{N}$$

Quantities given

$$\kappa = \frac{1}{R} \times \text{cell constant} = \frac{1}{380} \times 3.87 = 0.01018 \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$N = 0.1$$

Substitution of values

$$\begin{aligned} \Lambda &= \frac{0.01018 \times 1000}{0.1} \text{ ohm}^{-1} \text{ cm}^2 \text{ eqvt}^{-1} \\ &= 101.8 \text{ ohm}^{-1} \text{ cm}^2 \text{ eqvt}^{-1} \end{aligned}$$

SOLVED PROBLEM 17. A solution of silver nitrate containing 6.07 g silver in 25 ml solution was electrolysed between platinum electrodes. After electrolysis, 5.77 g of silver was present in 25 ml of anode solution while 0.625 g of metallic silver was deposited on the cathode. Calculate the transport number of Ag^+ and NO_3^- ions.

SOLUTION : (i) To calculate the transport no. of Ag^+ ions**Formula used**

$$\text{Transport number of } \text{Ag}^+ \text{ ions} = \frac{\text{Fall in conc. around anode}}{\text{No. of g eqvt deposited in silver coulometer}}$$

Quantities given

$$\text{Fall in conc. around anode} = 6.07 - 5.77 \text{ g} = 0.3 \text{ g} = \frac{0.3}{108} \text{ g eqvt.} = 0.002777 \text{ g eqvt.}$$

$$\text{No. of eqvt. deposited in silver coulometer} = \frac{0.625}{108} = 0.005787 \text{ g eqvt.}$$

Substitution of values

$$\begin{aligned}\text{Transport number of Ag}^+ \text{ ions} &= \frac{0.002777}{0.005787} \\ &= 0.4799\end{aligned}$$

(ii) To calculate the transport number of NO_3^- ions.

$$\begin{aligned}\text{Transport number of } \text{NO}_3^- \text{ ions} &= 1 - \text{transport no. of Ag}^+ \text{ ions} \\ &= 1 - 0.479 \\ &= \mathbf{0.529}\end{aligned}$$

SOLVED PROBLEM 18. Ratio of Ag^+ and NO_3^- ions in the solution of AgNO_3 electrolysed between silver electrodes is 0.75. Find the transport number of the two ions.

SOLUTION :**Formula used**

$$t_{\text{NO}_3^-} = \frac{\mu_{\text{NO}_3^-}}{\mu_{\text{NO}_3^-} + \mu_{\text{Ag}^+}}$$

Quantity given

$$\frac{\mu_{\text{Ag}^+}}{\mu_{\text{NO}_3^-}} = 0.75 \quad \text{or} \quad 1 + \frac{\mu_{\text{Ag}^+}}{\mu_{\text{NO}_3^-}} = 1.75$$

Substitution of values

$$\begin{aligned}t_{\text{NO}_3^-} &= \frac{1}{1.75} = \mathbf{0.571} \\ t_{\text{Ag}^+} &= 1 - t_{\text{NO}_3^-} \\ &= 1 - 0.571 \\ &= \mathbf{0.429}\end{aligned}$$

SOLVED PROBLEM 19. In a moving boundary method, a current of 25 mA was passed for 80 seconds. During this time the boundary of a solution of HCl containing 0.01 mol dm^{-3} moved 16.8 cm towards the cathode. Calculate the transport number of H^+ and Cl^- ions. The cross-sectional area of the glass tube is $1.00 \times 10^{-5} \text{ m}^2$.

SOLUTION :**Formula used**

$$t_{\text{H}^+} = \frac{s \times l \times c}{n}$$

Quantities given

$$l = 16.8 \text{ cm} = 16.8 \times 10^{-2} \text{ m}$$

$$s = 1.0 \times 10^{-5} \text{ m}^2$$

$$c = 0.01 \text{ mol dm}^{-3}$$

$$n = \frac{Q}{F} = \frac{25 \times 10^{-3} \times 80}{96500}$$

Substitution of values

$$\begin{aligned}t_{\text{H}^+} &= \frac{16.8 \times 10^{-2} \text{ m} \times 1.0 \times 10^{-5} \text{ m}^2 \times 0.01 \text{ mol dm}^{-3}}{\frac{25 \times 10^{-3} \times 80}{96500} \times 1000} \\ &= \mathbf{0.81} \\ \text{and} \quad t_{\text{Cl}^-} &= 1 - t_{\text{H}^+} \\ &= 1 - 0.81 \\ &= \mathbf{0.19}\end{aligned}$$

ADDITIONAL PRACTICE PROBLEMS

- A solution of HCl was electrolysed in a transference cell, between two platinum electrodes. The electrode compartment contained 0.354 g of chloride ions before electrolysis and 0.326 g after electrolysis. A silver coulometer in series had a deposit of 0.532 g of silver after passing the same amount of current. Calculate the transport number of H^+ and Cl^- ions.

Answer. 0.16 and 0.84
- In an electrolysis of copper sulphate between copper electrodes, the total mass of copper deposited at the cathode was 0.153 g and masses of copper per unit volume of the anode liquid after and before electrolysis are 0.91 and 0.79 g respectively. Calculate the transport number of Cu^{2+} and SO_4^{2-} ions.

Answer. 0.215 and 0.785
- In the Hittorf cell using silver electrodes and AgNO_3 as an electrolyte, a certain amount of current was passing which deposited 9.886×10^{-4} g equivalent of silver in the coulometer. The anode compartment had the composition 28.235 g of H_2O and 0.099 g of AgNO_3 before electrolysis and 28.435 g of water and 0.1874 g of AgNO_3 after electrolysis. Calculate the transport number of Ag^+ and NO_3^- ions.

Answer. 0.48 and 0.52
- The ionic conductances of Li^+ , Na^+ and K^+ are 38.6, 50.1 and 73.5 $\text{ohm}^{-1} \text{cm}^2 \text{eqvt}^{-1}$ respectively. Calculate ionic mobilities.

Answer. 4×10^{-4} , 5.2×10^{-4} and 7.6×10^{-4}
- The equivalent conductivity of KCl at infinite dilution is 120 $\text{ohm}^{-1} \text{cm}^2 \text{eqvt}^{-1}$. The transport number of Cl^- ion in KCl at the same temperature is 0.51. Calculate the limiting ionic mobility and ionic conductance of K^+ ions.

Answer. 58.8 $\text{ohm}^{-1} \text{cm}^2 \text{eqvt}^{-1}$, $6.09 \times 10^{-4} \text{cm}^2 \text{s}^{-1} \text{v}^{-1}$
- A conductivity cell whose cell constant is 2 cm^{-1} , is filled with 0.1 M acetic acid solution. Its resistance is found to be 3765 ohm^{-1} . Calculate the degree of dissociation of acetic acid.

Answer. 0.0136
- A solution of HCl was electrolysed in a cell between two platinum electrodes. The cathode compartment contained 0.354 g of chloride ions before electrolysis and 0.32 g after electrolysis. A silver coulometer in series had a deposit of 0.532 g of silver after passing the same amount of current. Calculate the transport number of H^+ and Cl^- ions.

Answer. 0.84 ; 0.160
- In a moving boundary method, a current of 30 mA was passed for 80 seconds. During this time the boundary of a solution of HCl containing 0.01 mol dm^{-3} moved 17.0 cm towards the cathode. Calculate the transport number of H^+ and Cl^- ions. (The cross-sectional area of the glass tube is $1.0 \times 10^{-5} \text{m}^2$).

Answer. 0.68 ; 0.32
- The ionic equivalent conductances of Na^+ and Cl^- ions in 0.1 molar sodium chloride are 45 and 63 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$. What are their ionic mobilities and transport numbers ?

Answer. 4.66×10^{-4} and 6.53×10^{-4} , 0.417 and 0.583
- In a moving boundary experiment with 1 N KCl solution using CaCl_2 as indicator, a current of 0.0115 A was passed for half an hour and the boundary moved through a volume of 0.106 ml. Calculate the transport number of K^+ ion.

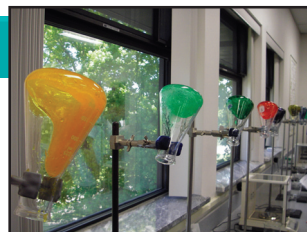
Answer. 0.494

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Ionic Equilibria Solubility Product

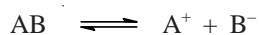
CHAPTER

KEY CONCEPTS AND EQUATIONS



THE OSTWALD'S DILUTION LAW

The law of Mass action can also be applied to the ionic equilibrium



The Dissociation constant or Ionisation constant for such an equilibrium is given by

$$K_c = \frac{\alpha^2 c}{(1 - \alpha)}$$

where α is the degree of dissociation and c is the concentration of the electrolyte. The above expression can also be written as

$$K_c = \frac{\alpha^2}{(1 - \alpha) V}$$

where V is volume of solution in litres containing 1 mole of an electrolyte. This expression is called Ostwald's Dilution Law. It reduces to

$$K_c = \frac{\alpha^2}{V}$$

for weak electrolytes when $1 - \alpha \cong 1$.

DEGREE OF DISSOCIATION

The fraction of the amount of the electrolyte in solution present as free ions is called the degree of dissociation. It is given by

$$x = \frac{\text{Amount dissociated (mol lit}^{-1}\text{)}}{\text{Initial concentration (mol lit}^{-1}\text{)}}$$

COMMON ION EFFECT

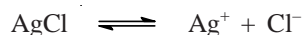
The reduction of the degree of dissociation of a salt by the addition of a common ion is called the common-ion effect.

SOLUBILITY EQUILIBRIA AND THE SOLUBILITY PRODUCT

A saturated solution is a solution in which the dissolved and undissolved solute are in equilibrium and the solubility of a substance in a solvent is the concentration in the saturated solution.

The molar solubility is defined as the number of moles of the substance per litre of solution.

For the equilibrium



we have

$$K = \frac{[\text{Ag}^+][\text{Cl}^-]}{[\text{AgCl}]}$$

In the saturated solution $[\text{AgCl}]$ does not change with time and the equilibrium expression becomes

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

where K_{sp} is called the solubility product and the product $[\text{Ag}^+][\text{Cl}^-]$ is called Ionic product.

CALCULATION OF K_{sp} FROM SOLUBILITY AND VICE VERSA

The K_{sp} expressions for various sparingly soluble salts are given in Table 26.1

TABLE 26.1 K_{sp} EXPRESSIONS FOR VARIOUS SALTS			
Salt	Formula	K_{sp}	
Silver Chloride	AgCl	$[\text{Ag}^+][\text{Cl}^-]$	$= s^2$
Barium Fluoride	BaF_2	$[\text{Ba}^{2+}][\text{F}^-]^2$	$= 4s^3$
Silver Chromate	Ag_2CrO_4	$[\text{Ag}^+]^2[\text{CrO}_4^{2-}]$	$= 4s^3$
Lead sulphate	PbSO_4	$[\text{Pb}^{2+}][\text{SO}_4^{2-}]$	$= s^2$

Knowing the value of K_{sp} , the solubility, s of the salt can be calculated.

PREDICTING WHETHER PRECIPITATION WILL OCCUR ON MIXING

When two reacting solutions are mixed, the ionic product Q is calculated from the concentration of the reacting ions. Following two cases arise

$$\begin{array}{ll} Q > K_{sp} & \text{precipitation occurs} \\ Q < K_{sp} & \text{No precipitation occurs} \end{array}$$

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. The solubility product of lead bromide is 8.0×10^{-5} . If the salt is 80% dissociated in the saturated solution, find the solubility of the salt.

SOLUTION :



Formula used

$$K_{sp} = [\text{Pb}^{2+}][\text{Br}^-]^2$$

Quantity given

$$K_{sp} = 8.0 \times 10^{-5}$$

Substitution of values

$$8.0 \times 10^{-5} = s(\text{mol lit}^{-1}) \times [2s(\text{mol lit}^{-1})]^2$$

or

$$4s^3 = 8.0 \times 10^{-5}$$

or

$$\begin{aligned} s &= \sqrt[3]{2.0 \times 10^{-5}} \\ &= 2.714 \times 10^{-2} \text{ mol lit}^{-1} \end{aligned}$$

If the salt is 80% dissociated, the solubility is

$$\begin{aligned}
 &= \frac{2.714 \times 10^{-2} \times 80}{100} = 2.171 \times 10^{-2} \text{ mol lit}^{-1} \\
 &= 2.17 \times 10^{-2} \times 368 \text{ g lit}^{-1} \\
 &= \mathbf{7.9856 \text{ g lit}^{-1}}
 \end{aligned}$$

SOLVED PROBLEM 2. The solubility of silver chloride at 25 °C is 1.05×10^{-5} moles per litre. Calculate the solubility product.

SOLUTION :

Formula used

$$K_{sp} = [Ag^+] [Cl^-]$$

Quantities given

$$[Ag^+] = 1.05 \times 10^{-5} \text{ mole per litre}$$

$$[Cl^-] = 1.05 \times 10^{-5} \text{ mole per litre}$$

Substitution of values

$$\begin{aligned}
 K_{sp} &= 1.05 \times 10^{-5} \times 1.05 \times 10^{-5} \\
 &= \mathbf{1.1025 \times 10^{-10}}
 \end{aligned}$$

SOLVED PROBLEM 3. The solubility of $BaSO_4$ at 18 °C is 0.00233 g per litre. Calculate the solubility product of $BaSO_4$. (Molecular weight of $BaSO_4$ is 233)

SOLUTION :

Formula used

$$K_{sp} = [Ba^{2+}] [SO_4^{2-}]$$

Quantities given

$$[SO_4^{2-}] = [Ba^{2+}] = 0.00233 \text{ g lit}^{-1} = \frac{0.00233}{233} \text{ mol lit}^{-1} = 1 \times 10^{-3} \text{ mol lit}^{-1}$$

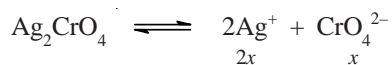
Substitution of values

$$\begin{aligned}
 K_{sp} &= (1.0 \times 10^{-3}) \times (1.0 \times 10^{-3}) \\
 &= \mathbf{1.0 \times 10^{-6}}
 \end{aligned}$$

SOLVED PROBLEM 4. The solubility product of silver chromate is 2.0×10^{-12} at 25 °C. Calculate the solubility at this temperature.

SOLUTION :

The equilibrium reaction is



Equilibrium concentration

Formula used

$$\begin{aligned}
 K_{sp} &= [Ag^+]^2 [CrO_4^{2-}] \\
 &= (2x)^2 (x) \\
 &= 4x^3
 \end{aligned}$$

Quantities given

$$K_{sp} = 2.0 \times 10^{-12}$$

Substitution of values

$$2.0 \times 10^{-12} = 4x^3$$

or

$$\begin{aligned}
 x &= \sqrt[3]{\frac{2.0 \times 10^{-12}}{4}} \\
 &= \mathbf{7.937 \times 10^{-5} \text{ mole lit}^{-1}}
 \end{aligned}$$

SOLVED PROBLEM 5. At 20 °C the solubility of silver chloride in water is 1.435×10^{-3} g per litre.

Find the solubility of AgCl.

SOLUTION :



Formula used

$$K_{sp} = [\text{Ag}^+] [\text{Cl}^-] = s^2$$

Quantity given

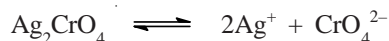
$$s = 1.435 \times 10^{-3} \text{ g lit}^{-1} = \frac{1.435 \times 10^{-3}}{143.5} \text{ mol lit}^{-1} \\ = 1 \times 10^{-5} \text{ mol lit}^{-1}$$

Substitution of values

$$K_{sp} = (1 \times 10^{-5}) \times (1 \times 10^{-5}) \\ = 1 \times 10^{-10}$$

SOLVED PROBLEM 6. The solubility of Ag_2CrO_4 (m. wt = 332) is 0.024 gram lit^{-1} . Find the solubility product.

SOLUTION :



Formula used

$$K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}] \\ = (2s)^2 \times s = 4s^3$$

Quantity given

$$s = 0.024 \text{ g lit}^{-1} = \frac{0.024}{332} \text{ mol lit}^{-1} = 7.2289 \times 10^{-5} \text{ mol lit}^{-1}$$

Substitution of value

$$K_{sp} = 4 \times (7.2289 \times 10^{-5})^3 \\ = 1.511 \times 10^{-12}$$

SOLVED PROBLEM 7. Calculate the pH value of a solution obtained by mixing 500 ml of 0.1 N CH_3COOH and 500 ml of 0.1 N CH_3COONa . K_a for acetic acid is 1.8×10^{-5} .

SOLUTION :

Formula used

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

Quantities given

$$\text{p}K_a = -\log 1.8 \times 10^{-5} = 4.774$$

$$[\text{Salt}] = \frac{0.1}{2} = 0.05 \text{ N}$$

$$[\text{Acid}] = \frac{0.1}{2} = 0.05 \text{ N}$$

Substitution of values

$$\text{pH} = 4.774 + \log \frac{0.05}{0.05} \\ = 4.774$$

SOLVED PROBLEM 8. The dissociation constants for formic acid and acetic acid are 21.4×10^{-5} and 1.8×10^{-5} respectively. What are the relative strengths of the two acids ?

SOLUTION :**Formula used**

$$\frac{\text{Strength of HCOOH}}{\text{Strength of CH}_3\text{COOH}} = \sqrt{\frac{K_{\text{HCOOH}}}{K_{\text{CH}_3\text{COOH}}}}$$

Quantities given

$$K_1 = 21.4 \times 10^{-5}$$

$$K_2 = 1.8 \times 10^{-5}$$

Substitution of values

$$\begin{aligned} \frac{\text{Strength of HCOOH}}{\text{Strength of CH}_3\text{COOH}} &= \sqrt{\frac{21.4 \times 10^{-5}}{1.8 \times 10^{-5}}} \\ &= \mathbf{3.448} \end{aligned}$$

Thus formic acid is 3.448 times stronger than the acetic acid.

SOLVED PROBLEM 9. Calculate the *pH* value of a solution whose hydrogen ion concentration is 0.006 gm ion/litre.

SOLUTION :**Formula used**

$$pH = -\log [H^+]$$

Quantity given

$$[H^+] = 0.006 \text{ g lit}^{-1} = \frac{0.006}{2} \text{ mol lit}^{-1} = 0.003 \text{ mol lit}^{-1}$$

Substitution of values

$$\begin{aligned} pH &= -\log (0.003) \\ &= -\log (3 \times 10^{-3}) \\ &= (3 - 0.4771) \\ &= \mathbf{2.5229} \end{aligned}$$

SOLVED PROBLEM 10. What is the *pH* of the buffer composed of 0.1M solution of HCN in 0.1M KCN ? The dissociation constant of HCN is 0.01.

SOLUTION :**Formula used**

$$pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

Quantities given

$$pK_a = -\log K_a = -\log 0.01 = 1.6990$$

$$[\text{Salt}] = 0.1 \text{ M}$$

$$[\text{Acid}] = 0.1 \text{ M}$$

Substitution of values

$$\begin{aligned} pH &= 1.6990 + \log \frac{0.1}{0.1} \\ &= \mathbf{1.6990} \end{aligned}$$

SOLVED PROBLEM 11. Calculate the *pH* of (i) 10^{-8} N aqueous HCl solution ; and (ii) 10^{-7} N aqueous NaOH solution.

SOLUTION : (i) 10^{-8} N aqueous HCl solution**Formula used**

$$pH = -\log [H^+]$$

Quantity given

$$[H^+] = 10^{-8}$$

Substitution of values

$$\begin{aligned} pH &= -\log(10^{-8}) \\ &= 8 \end{aligned}$$

(ii) 10^{-7} N aqueous NaOH solution

Formula used

$$pH = -\log[H^+]$$

Quantity given

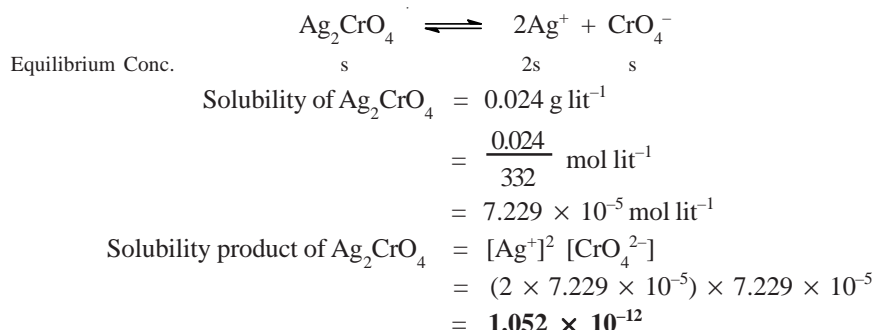
$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{10^{-7}} = 10^{-7}$$

Substitution of values

$$\begin{aligned} pH &= -\log(10^{-7}) \\ &= 7 \end{aligned}$$

SOLVED PROBLEM 12. The solubility of Ag_2CrO_4 (mol. mass = 332) is 0.024 g lit^{-1} . Find the solubility product.

SOLUTION : The solubility equilibrium is



SOLVED PROBLEM 13. The specific conductivity of a saturated solution of silver chloride is 1.33×10^{-6} mhos at 25°C . Given that the ionic conductivities for Ag^+ and Cl^- ions are 56.9 and 68.4 mhos respectively. Calculate the solubility and solubility product of silver chloride.

SOLUTION : To calculate the solubility of AgCl.

Formula used

$$\lambda_\infty = \kappa \times V$$

Quantities given

$$\lambda_\infty = \Lambda_{Ag^+} + \Lambda_{Cl^-} = 56.9 + 68.4 = 125.3 \quad \kappa = 1.33 \times 10^{-6}$$

Substitution of values

$$125.3 = 1.33 \times 10^{-6} \times V$$

or

$$V = \frac{125.3}{1.33 \times 10^{-6}} = 94.2 \times 10^6 \text{ cm}^3$$

$$94.2 \times 10^6 \text{ cm}^3 \text{ contain AgCl} = 1 \text{ g equivalent} = 143.5 \text{ g AgCl}$$

$$\begin{aligned} 1000 \text{ cm}^3 \text{ contain AgCl} &= \frac{143.5 \times 1000}{94.2 \times 10^6} \\ &= \mathbf{1.523 \times 10^{-3} \text{ g lit}^{-1}} \end{aligned}$$

(ii) To calculate the solubility product of AgCl

Formula used

$$K_{sp} = [Ag^+] [Cl^-]$$

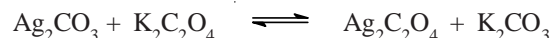
Quantities given

$$[Ag^+] = [Cl^-] = \frac{1.523 \times 10^{-3} \text{ g lit}^{-1}}{143.5 \text{ g lit}^{-1}} = 1.06 \times 10^{-5} \text{ mol lit}^{-1}$$

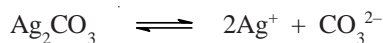
Substitution of values

$$\begin{aligned} K_{sp} &= (1.06 \times 10^{-5}) (1.06 \times 10^{-5}) \\ &= \mathbf{1.1236 \times 10^{-10}} \end{aligned}$$

SOLVED PROBLEM 14. The solubility product of Ag_2CrO_4 at $25^\circ C$ is $1.29 \times 10^{-11} \text{ mol lit}^{-3}$. A solution of $K_2C_2O_4$ containing 0.1520 mole in 500 ml water is shaken with excess of Ag_2CO_3 till the following equilibrium is reached :



At equilibrium the solution contains 0.0358 mole of K_2CO_3 . Assuming the degree of dissociation of $K_2C_2O_4$ and K_2CO_3 to be equal, calculate the solubility product of Ag_2CO_3 .

SOLUTION :

$$K_{sp}(Ag_2C_2O_4) = [Ag^+]^2 [C_2O_4^{2-}]$$

$$\text{or} \quad [Ag^+]^2 = \frac{K_{sp}[Ag_2C_2O_4]}{[C_2O_4^{2-}]} \quad \dots(i)$$

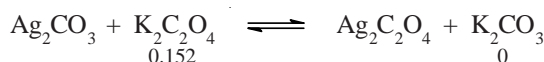
$$\text{and} \quad K_{sp}(Ag_2CO_3) = [Ag^+]^2 [CO_3^{2-}]$$

$$\text{or} \quad [Ag^+]^2 = \frac{K_{sp}[Ag_2CO_3]}{[CO_3^{2-}]} \quad \dots(ii)$$

Since the concentration $[Ag^+]$ is the same in equations (i) and (ii) we have

$$\frac{K_{sp}[Ag_2C_2O_4]}{[C_2O_4^{2-}]} = \frac{K_{sp}[Ag_2CO_3]}{[CO_3^{2-}]} \quad \dots (iii)$$

The chemical reaction between Ag_2CO_3 and $K_2C_2O_4$ is



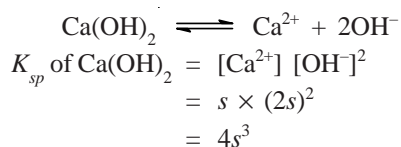
Initial Conc.	0.152	0
Conc. at Equilibrium	$0.152 - 0.0358$	0.0358
equilibrium conc. (mol lit^{-1})	0.2324	0.0716

Substituting the values in equation (iii) we have

$$\begin{aligned} K_{sp}[Ag_2CO_3] &= \frac{K_{sp}[Ag_2C_2O_4] \times [C_2O_4^{2-}]}{[CO_3^{2-}]} \\ &= \frac{1.29 \times 10^{-11} \text{ mol}^3 \text{ lit}^{-3} \times 0.0716 \text{ mol lit}^{-1}}{0.2324 \text{ mol lit}^{-1}} \\ &= \mathbf{3.97 \times 10^{-12} \text{ mol}^3 \text{ lit}^{-3}} \end{aligned}$$

SOLVED PROBLEM 15. The solubility product K_{sp} of Ca(OH)_2 at 298 K is 4.42×10^{-5} . 500 ml of a saturated solution of Ca(OH)_2 is mixed with equal volume of 0.4 M NaOH. How much Ca(OH)_2 in milligram is precipitated?

SOLUTION : The ionisation of Ca(OH)_2 is represented as



or

$$\begin{aligned}s &= \sqrt[3]{\frac{K_{sp}}{4}} \\ &= \sqrt[3]{\frac{4.42 \times 10^{-5}}{4}} \\ &= 2.227 \times 10^{-2} \text{ M}\end{aligned}$$

$$\begin{aligned}\text{No. of moles of } \text{Ca}^{2+} \text{ ions in 500 ml of the solution} &= \frac{2.227 \times 10^{-2}}{2} \\ &= 0.011135\end{aligned}$$

When 500 ml of saturated solution is mixed with 500 ml of 0.4 M NaOH the resultant volume is 1000 ml. The molarity of OH^- ions in the resultant solution becomes 0.2 M

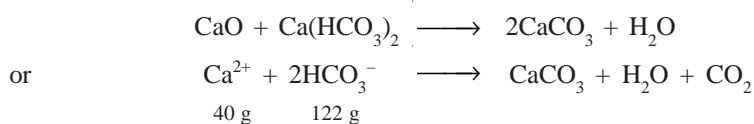
$$\begin{aligned}\text{Now} \quad [\text{Ca}^{2+}] &= \frac{K_{sp}}{[\text{OH}^-]^2} \\ &= \frac{4.42 \times 10^{-5}}{0.2 \times 0.2} \\ &= 0.001105 \text{ M}\end{aligned}$$

$$\begin{aligned}\text{No. of moles of } \text{Ca}^{2+} \text{ ions or } \text{Ca(OH)}_2 \text{ precipitated} &= \text{Initial conc. of } \text{Ca}^{2+} - \text{Final conc. of } \text{Ca}^{2+} \\ &= 0.011135 - 0.001105 \\ &= 0.010245 \text{ M}\end{aligned}$$

$$\begin{aligned}\text{Thus the mass of } \text{Ca(OH)}_2 \text{ precipitated} &= 0.010245 \times 74 \\ &= 0.75813 \text{ g} \\ &= \mathbf{758.13 \text{ mg}}\end{aligned}$$

SOLVED PROBLEM 16. A sample of hard water contains 96 ppm of SO_4^{2-} and 183 ppm of HCO_3^- , with Ca^{2+} as the only cation. How many moles of CaO will be required to remove HCO_3^- from 1000 kg of this water? If 1000 kg of this water is treated with the amount of CaO calculated above, what will be the concentration (in ppm) of residual Ca^{2+} ions? (Assume CaCO_3 to be completely insoluble in water). If the Ca^{2+} ions in one litre of the treated water are completely exchanged with hydrogen ions, what will be its pH?

SOLUTION : The reactions are



122 g of HCO_3^- ions are precipitated by = 40 g of Ca^{2+} ions

$$\therefore 183 \text{ g of } \text{HCO}_3^- \text{ ions are precipitated by } = \frac{40 \times 183}{122} \text{ g of } \text{Ca}^{2+} \text{ ions}$$

$$= 60 \text{ g of } \text{Ca}^{2+} \text{ ions}$$

But 40 g of Ca^{2+} ions are present in = 56 g of CaO

and 60 g of Ca^{2+} ions are present in = $\frac{56 \times 60}{40}$ g of CaO

$$= 84 \text{ g of CaO}$$

$$\text{No. of moles of CaO in 84 g of CaO} = \frac{84 \text{ g}}{56 \text{ g mol}^{-1}} = 1.5 \text{ mol}$$

96 ppm of SO_4^{2-} = 96 ppm of Ca^{2+} ions

$$\therefore \text{Conc. of } \text{CaSO}_4 = 96 \text{ ppm}$$

$$= \frac{96}{136}$$

$$= 0.706 \text{ mol of } \text{CaSO}_4$$

$$= \mathbf{0.706 \times 10^{-3} \text{ mol lit}^{-1}}$$

\therefore when 0.706×10^{-3} mol in 1 litre Ca^{2+} ions exchanged with H^+ ions of water

$$\text{Concentration of } \text{H}^+ \text{ ions} = 2 \times 0.706 \times 10^{-3} \text{ mol lit}^{-1}$$

$$= 1.412 \times 10^{-3} \text{ mol lit}^{-1}$$

or Concentration of OH^+ ions = $1.412 \times 10^{-3} \text{ mol lit}^{-1}$

$$pOH = -\log [\text{OH}^-]$$

$$= -\log (1.412 \times 10^{-3})$$

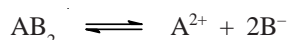
$$= 2.85$$

$$pH = 14 - pOH = 14 - 2.85$$

$$= \mathbf{11.15}$$

SOLVED PROBLEM 17. The solubility of a salt of type AB_2 with mol mass 78 in water is $1.6 \times 10^{-2} \text{ g lit}^{-1}$ at 20°C . Calculate its solubility product.

SOLUTION : The equilibrium is



The solubility of the salt AB_2 in moles per litre

$$= \frac{1.6 \times 10^{-2} \text{ g lit}^{-1}}{78 \text{ g mol}^{-1}}$$

$$= 2.05 \times 10^{-4} \text{ mol lit}^{-1}$$

Formula used

$$K_{sp} = [\text{A}^{2+}] [\text{B}^-]^2$$

Quantities given

$$[\text{A}^{2+}] = 2.05 \times 10^{-4} \text{ mol lit}^{-1}$$

$$[\text{B}^-] = 2 \times 2.05 \times 10^{-4} \text{ mol lit}^{-1}$$

$$= 4.1 \times 10^{-4} \text{ mol lit}^{-1}$$

Substitution of values

$$K_{sp} = 2.05 \times 10^{-4} \times (4.1 \times 10^{-4})^2$$

$$= \mathbf{3.446 \times 10^{-11}}$$

ADDITIONAL PRACTICE PROBLEMS

- A sample of hard water contains 0.005 mole of CaCO_3 per litre. What is the minimum concentration of Na_2SO_4 which must be exceeded for removing the calcium ions from this water sample? The solubility product constant of calcium sulphate at 25°C is 2.40×10^{-5} .

Answer. greater than $0.0048 \text{ mol lit}^{-1}$
- When one litre of saturated solution of lead chloride, PbCl_2 is evaporated to dryness, the residue is found to weight 4.5 g. Calculate the value of K_{sp} for PbCl_2 .

Answer. 1.7×10^{-5}
- Calculate the solubility product of AgCl if its solubility at 20°C is $1.435 \times 10^{-5} \text{ g/litre}$.

Answer. 1×10^{-10}
- The solubility of Mg(OH)_2 in pure water is $9.57 \times 10^{-3} \text{ g lit}^{-1}$. Calculate its solubility (g lit^{-1}) in 0.02 M Mg(OH)_2 solution

Answer. $8.7 \times 10^{-4} \text{ g lit}^{-1}$
- Calculate the solubility product of $\text{AgCl}_{(s)}$ in pure water and in 0.1 M NaCl at 25°C .

$K_{sp}(\text{AgCl}) = 2.8 \times 10^{-10}$

Answer. $1.673 \times 10^{-5} \text{ mol lit}^{-1}$; $2.8 \times 10^{-9} \text{ mol lit}^{-1}$
- The solubility product of AgCl in water is 1.5×10^{-10} . Calculate its solubility in 0.01 M NaCl solution.

Answer. $1.5 \times 10^{-8} \text{ mol lit}^{-1}$
- Calculate the solubility product of silver chromate (molar mass 332) if at 25°C it requires 0.0435 g of Ag_2CrO_4 to form its one litre saturated solution.

Answer. 5.24×10^{-12}
- Calculate the solubility product of silver chromate Ag_2CrO_4 at 25°C if the concentration of Ag^+ ion $1.5 \times 10^{-4} \text{ mol lit}^{-1}$ is in a saturated solution of silver chromate at 25°C .

Answer. $K_{sp} = 1.6875 \times 10^{-12}$
- The solubility of lead sulphate in water 0.038 g lit^{-1} at 25°C . Calculate its solubility product at 25°C . (molar mass of $\text{PbSO}_4 = 303$).

Answer. 1.5725×10^{-8}
- The solubility product of BaSO_4 is 1.5×10^{-9} . Find out the solubility in pure water and in 0.1 M BaCl_2 solution.

Answer. $3.87 \times 10^{-5} \text{ mol lit}^{-1}$; $1.5 \times 10^{-8} \text{ mol lit}^{-1}$

27

Acids and Bases

CHAPTER

KEY CONCEPTS AND EQUATIONS



ARRHENIUS CONCEPTS

An acid is a compound that releases H^+ ions in water ; and a base is a compound that releases OH^- ions in water.

BRONSTED LOWRY CONCEPT

An acid is any molecule or ion that can donate a proton (H^+) and a base is any molecule or ion that can accept a proton.

LEWIS CONCEPT

An acid is a substance which accepts an electron pair and a base is a substance that donates an electron pair.

RELATIVE STRENGTH OF ACIDS AND BASES

The dissociation constant of an acid, HA, is given by

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

The value of K_a is a measure of $[H^+]$ or its acid strength.

The dissociation constant of a base, BOH, is given by

$$K_b = \frac{[B^+][OH^-]}{[BOH]}$$

The value of K_b is a measure of $[OH^-]$ or its strength.

THE pH OF SOLUTIONS

The pH is defined as the negative of logarithm of H^+ ion concentration. Mathematically,

$$pH = -\log [H^+]$$

Similarly for a base pOH is defined as the negative of logarithm of OH^- ion concentration. i.e.,

$$pOH = -\log [OH^-]$$

And for water

$$pK_w = -\log [K_w]$$

The pK_w is related to pH and pOH by the relation

$$pK_w = pH + pOH$$

BUFFER SOLUTION

A buffer solution is one which maintains its pH fairly even upon the addition of small amounts of acid or base. In other words, a buffer solution resists a change in its pH on the addition of a small amount of an acid or base.

The pH of a buffer solution is given by

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

or

$$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. Two hypothetical acids HA and HB have the dissociation constant 1×10^{-3} and 1×10^{-5} respectively in water at 25°C . Calculate the strength of HA with respect to HB.

SOLUTION :

Formula used

$$\frac{\text{Strength of acid HA}}{\text{Strength of acid HB}} = \sqrt{\frac{K_{HA}}{K_{HB}}}$$

Quantities given

$$K_{HA} = 1 \times 10^{-3}$$

$$K_{HB} = 1 \times 10^{-5}$$

Substitution of values

$$\begin{aligned} \frac{\text{Strength of acid HA}}{\text{Strength of acid HB}} &= \sqrt{\frac{1 \times 10^{-3}}{1 \times 10^{-5}}} \\ &= \sqrt{1 \times 10^2} \\ &= 10 \end{aligned}$$

Thus, acid HA is 10 times stronger than HB.

SOLVED PROBLEM 2. Dissociation constant of propionic acid at 25°C is 1.34×10^{-5} . Calculate the degree of dissociation and pH in 0.1 M acid.

SOLUTION : (i) To calculate the degree of dissociation of propionic acid

Formula used

$$K_a = \frac{\alpha^2 C}{1 - \alpha} \quad \text{or} \quad \alpha^2 C \quad [\because 1 - \alpha \approx 1]$$

Quantities given

$$K_a = 1.34 \times 10^{-5}$$

$$C = 0.1 \text{ M}$$

Substitution of values

$$1.34 \times 10^{-5} = \alpha^2 \times 0.1$$

or

$$\alpha^2 = \frac{1.34 \times 10^{-5}}{0.1}$$

or

$$\begin{aligned} \alpha &= \sqrt{1.34 \times 10^{-4}} \\ &= 0.0115 \end{aligned}$$

(ii) To calculate the pH of 0.1 M propionic acid

Formula used

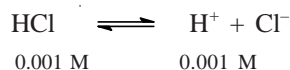
$$pH = -\log [H^+]$$

Quantities given

$$[H^+] = 0.0115 \text{ M}$$

Substitution of value

$$\begin{aligned} pH &= -\log(0.0115) \\ &= \mathbf{1.939} \end{aligned}$$

SOLVED PROBLEM 3. Calculate the *pH* of 0.001 N HCl assuming complete ionisation of HCl.**SOLUTION :****Formula used**

$$pH = -\log [H^+]$$

Quantities given

$$[H^+] = 0.001 \text{ N}$$

Substitution of value

$$\begin{aligned} pH &= -\log(0.001) \\ &= \mathbf{3} \end{aligned}$$

SOLVED PROBLEM 4. Given the dissociation constant of acetic acid at 25 °C as 1.8×10^{-5} , calculate the *pH* of a solution containing 0.185 mol acetic acid and 3.015 g mol sodium acetate per litre.**SOLUTION :****Formula used**

$$pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

Quantities given

$$pK_a = -\log(1.8 \times 10^{-5}) = 4.7447$$

$$[\text{Salt}] = 3.015 \text{ M}$$

$$[\text{Acid}] = 0.185 \text{ M}$$

Substitution of values

$$\begin{aligned} pH &= 4.7447 + \log \frac{3.015}{0.185} \\ &= 4.7447 + \log 16.297 \\ &= 4.7447 + 1.2121 \\ &= \mathbf{5.9568} \end{aligned}$$

SOLVED PROBLEM 5. Calculate *pH* of 0.085 N monobasic acid which dissociates 25%.**SOLUTION : (i) To calculate the concentration of $[H^+]$ ions.**Since the acid is 25% dissociated, the concentration of H^+ will be

$$\begin{aligned} [H^+] &= \frac{25}{100} \times 0.085 \text{ M} \\ [H^+] &= 0.02125 \text{ M} \end{aligned}$$

(ii) To calculate the *pH* value**Formula used**

$$pH = -\log [H^+]$$

Quantity given

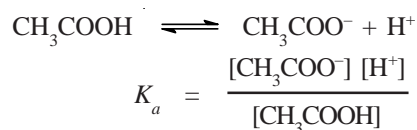
$$[H^+] = 0.02125 \text{ M}$$

Substitution of values

$$\begin{aligned} pH &= -\log(0.02125) \\ &= \mathbf{1.6726} \end{aligned}$$

SOLVED PROBLEM 6. Calculate the pH of a 0.1 M acetic acid when it is half neutralised by NaOH solution ($K_a = 1.7 \times 10^{-5}$).

SOLUTION : Acetic acid dissociates as



Let x be the concentration of H^+ ions at equilibrium, then

$$\begin{aligned} [\text{H}^+] &= [\text{CH}_3\text{COO}^-] = x \\ [\text{CH}_3\text{COOH}] &= 0.05 - x \approx 0.05 \end{aligned}$$

Substituting the values we get

$$K_a = \frac{x \times x}{0.05}$$

Quantity given

$$K_a = 1.7 \times 10^{-5}$$

Substitution of values

$$1.7 \times 10^{-5} = \frac{x^2}{0.05}$$

or

$$x^2 = 8.5 \times 10^{-7}$$

or

$$x = 9.219 \times 10^{-4}$$

Now

$$\begin{aligned} pH &= -\log[\text{H}^+] \\ &= -\log(9.219 \times 10^{-4}) \\ &= \mathbf{3.0353} \end{aligned}$$

SOLVED PROBLEM 7. Calculate the pH of the buffer solution containing 0.04 M NH_4Cl and 0.02 M NH_4OH . K_b for NH_4OH is 1.8×10^{-5} .

SOLUTION :

Formula used

$$pOH = pK_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

Quantities given

$$pK_b = -\log 1.8 \times 10^{-5} = 4.7447 \quad [\text{Salt}] = 0.04 \text{ M} \quad [\text{Base}] = 0.02 \text{ M}$$

Substitution of values

$$\begin{aligned} pOH &= 4.7447 + \log \frac{0.04}{0.02} \\ &= 4.7447 + \log 2 \\ &= 4.7447 + 0.3010 \\ &= 5.0457 \end{aligned}$$

Since

$$\begin{aligned} pH + pOH &= 14 \\ pH &= 14 - pOH \\ &= 14 - 5.0457 \\ &= \mathbf{8.9543} \end{aligned}$$

SOLVED PROBLEM 8. A buffer solution is prepared by mixing 3 g of acetic acid and 1.30 g of sodium acetate ($\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$) and making the total volume to one litre. Calculate the pH of the buffer. ($K_a = 1.8 \times 10^{-5}$; $H = 1$; $C = 12$; $O = 16$; $Na = 23$)

SOLUTION :**Formula used**

$$pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

Quantities given

$$pK_a = -\log K_a = -\log (1.8 \times 10^{-5}) = 4.7447$$

$$[\text{Salt}] = \frac{1.30}{136} = 9.559 \times 10^{-3} \text{ M} \qquad [\text{Acid}] = \frac{3}{60} = 0.05 \text{ M}$$

Substitution of values

$$\begin{aligned} pH &= 4.7447 + \log \frac{9.559 \times 10^{-3}}{0.05} \\ &= 4.7447 - 0.7185 \\ &= \mathbf{4.0262} \end{aligned}$$

SOLVED PROBLEM 9. Calculate the degree of hydrolysis of ammonium acetate. The dissociation constant of NH_4OH is 1.8×10^{-5} and that of acetic acid is 1.8×10^{-5} and $K_w = 1.0 \times 10^{-14}$.

SOLUTION :**Formula used**

$$K_h = \frac{K_w}{K_a K_b}$$

Quantities given

$$K_w = 1 \times 10^{-14}$$

$$K_a = 1.8 \times 10^{-5}$$

$$K_b = 1.8 \times 10^{-5}$$

Substitution of values

$$\begin{aligned} K_h &= \frac{1 \times 10^{-14}}{1.8 \times 10^{-5} \times 1.8 \times 10^{-5}} \\ &= \mathbf{3.0864 \times 10^{-5}} \end{aligned}$$

SOLVED PROBLEM 10. Calculate the pH of solution having hydrogen ion concentration $2.5 \times 10^{-3} \text{ M}$.

Solution :**Formula used**

$$pH = -\log [H^+]$$

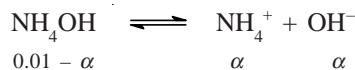
Quantity given

$$[H^+] = 2.5 \times 10^{-3} \text{ M}$$

Substitution of values

$$\begin{aligned} pH &= -\log (2.5 \times 10^{-3}) \\ &= -\log (0.0025) \\ &= -(-2.6020) \\ &= \mathbf{2.6020} \end{aligned}$$

SOLVED PROBLEM 11. Calculate the pH of 0.01 M NH_4OH solution. Dissociation constant of NH_4OH is 1.8×10^{-5} .

SOLUTION : (i) To calculate the concentration of OH^- ions.

Formula used

$$\begin{aligned}
 K_b &= \frac{[NH_4^+][OH^-]}{[NH_4OH]} \\
 &= \frac{\alpha^2}{0.01 - \alpha} \\
 &= \frac{\alpha^2}{0.01} \quad [\because 0.01 - \alpha \approx 0.01]
 \end{aligned}$$

or

$$\alpha = \sqrt{0.01 \times K_b}$$

Substitution of values

$$\alpha = \sqrt{0.01 \times 1.8 \times 10^{-5}}$$

or

$$\alpha = \sqrt{1.8 \times 10^{-7}}$$

$$[OH^-] = \alpha = 4.2426 \times 10^{-4}$$

(ii) To calculate pOH value**Formula used**

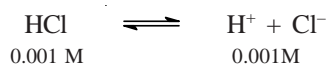
$$pOH = -\log [OH^-]$$

Quantity given

$$[OH^-] = 4.2426 \times 10^{-4}$$

Substitution of value

$$\begin{aligned}
 pH &= 14 - pOH \\
 &= 14 - 3.3723 \\
 &= \mathbf{10.6277}
 \end{aligned}$$

SOLVED PROBLEM 12. Calculate the pH of 0.001 M HCl and 0.01 M NaOH.**SOLUTION : (i) To calculate the pH of 0.001 M HCl****Formula used**

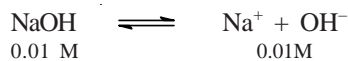
$$pH = -\log [H^+]$$

Quantity given

$$[H^+] = 0.001 \text{ M}$$

Substitution of value

$$\begin{aligned}
 pH &= -\log (0.001) \\
 &= \mathbf{3}
 \end{aligned}$$

(ii) To calculate pH of 0.01 M NaOH**Formula used**

$$pOH = -\log [OH^-]$$

Quantity given

$$[OH^-] = 0.01 \text{ M}$$

Substitution of value

$$pOH = -\log 0.01 = 2$$

Since

$$pH + pOH = 14$$

we have

$$pH = 14 - pOH$$

$$= 14 - 2$$

$$= 12$$

SOLVED PROBLEM 13. Calculate the pH volume of a solution obtained by mixing 0.083 mole of acetic acid and 0.091 mole of sodium acetate and making the volume 500 ml. K_a for acetic acid is 1.75×10^{-5} .

SOLUTION :

Formula used

$$pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

Quantities given

$$pK_a = -\log 1.75 \times 10^{-5} = 4.7569$$

$$[Salt] = 2 \times 0.091 \text{ M} = 0.182$$

$$[Acid] = 2 \times 0.083 \text{ M} = 0.166$$

Substitution of values

$$\begin{aligned} pH &= 4.7569 + \log \frac{0.182}{0.166} \\ &= 4.7569 + \log 1.0964 \\ &= 4.7569 + 0.0399 \\ &= \mathbf{4.7968} \end{aligned}$$

SOLVED PROBLEM 14. What will be the H^+ ion concentration of solutions having (i) $pH = 5.0$ and (ii) $pH = 7.8$?

SOLUTION :(i) To calculate the $[H^+]$ of solution having $pH = 5$

Formula used

$$pH = -\log [H^+]$$

or

$$[H^+] = \text{Antilog} (-pH)$$

Quantity given

$$pH = 5$$

Substitution of value

$$\begin{aligned} [H^+] &= \text{Antilog} (-5) \\ &= \mathbf{1 \times 10^{-5} \text{ M}} \end{aligned}$$

(ii) To calculate the $[H^+]$ of solution having $pH = 7.8$

Formula used

$$pH = -\log [H^+]$$

or

$$[H^+] = \text{Antilog} (-pH)$$

Quantity given

$$pH = 7.8$$

Substitution of value

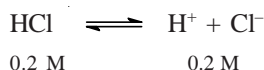
$$\begin{aligned} [H^+] &= \text{Antilog} -7.8 \\ &= \mathbf{1.584 \times 10^{-8}} \end{aligned}$$

SOLVED PROBLEM 15. What is pH of the solution when 0.20 mole of HCl is mixed to one litre of a solution containing

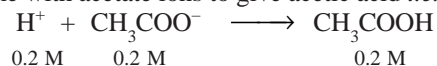
- (i) 1 M each of acetic acid and acetate ion.
- (ii) 0.1 M each acetic acid and acetate ion.

SOLUTION : (i) When 1 M each of acetic acid and acetate ion are mixed

$$\begin{aligned} [\text{CH}_3\text{COOH}] &= [\text{CH}_3\text{COONa}] = 1 \text{ M} & (\text{Given}) \\ \text{Amount of HCl added} &= 0.20 \text{ mole} \end{aligned}$$



H^+ ions combine with acetate ions to give acetic acid *i.e.*



The concentration of CH_3COOH will increase and it becomes 1.2 M and that of CH_3COO^- decreases to 0.8 M

Formula used

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

Quantities given

$$pK_a = -\log (1.8 \times 10^{-5}) = 4.7447 \quad [\text{Salt}] = 0.8 \text{ M} \quad [\text{Acid}] = 1.2 \text{ M}$$

Substitution of values

$$\begin{aligned} pH &= 4.7447 + \log \frac{0.8}{1.2} \\ &= 4.7447 + \log 0.667 \\ &= 4.7447 + (-0.1759) \\ &= \mathbf{4.5688} \end{aligned}$$

(ii) When 0.1 M each of acetic acid and acetate ion are mixed

$$[\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COONa}] = 0.1 \text{ M}$$

Out of 0.2 M HCl added 0.1 M will react with acetate ion to form 0.1 M of acetic acid. Thus the concentration of CH_3COOH would increase to $0.1 \text{ M} + 0.1 \text{ M} = 0.2 \text{ M}$

And in the presence of H^+ , the concentration of CH_3COOH does not increase. Thus pH of the solution will be due to the presence of H^+ ions of HCl *i.e.*

$$\begin{aligned} [\text{H}^+] &= 0.2 \text{ M} - 0.1 \text{ M} = 0.1 \text{ M} \\ pH &= -\log [\text{H}^+] \\ &= -\log (0.1) \\ &= \mathbf{1} \end{aligned}$$

SOLVED PROBLEM 16. How many moles of HCl will be required to prepare one litre of a buffer solution containing NaCN and HCl of pH 8.5 using 0.01 gram formula weight of NaCN ?

K (dissociation constant) of HCN = 4.1×10^{-10}

SOLUTION : The required $pH = 8.5$

$$pH = -\log [\text{H}^+]$$

$$\therefore \begin{aligned} [H^+] &= \text{Antilog}(-8.5) \\ &= 3.16 \times 10^{-9} \text{ M} \end{aligned}$$

This buffer solution can be prepared by mixing CN^- with HCN in proper proportions.

$$\begin{aligned} \text{HCN} &\rightleftharpoons \text{H}^+ + \text{CN}^- \\ K_w &= \frac{[H^+][\text{CN}^-]}{[\text{HCN}]} \\ \text{or} \quad \frac{[\text{CN}^-]}{[\text{HCN}]} &= \frac{K_w}{[H^+]} = \frac{4.1 \times 10^{-10}}{3.16 \times 10^{-9}} = 0.1294 \end{aligned}$$

The ratio of $[\text{CN}^-]$ to $[\text{HCN}]$ can be obtained by mixing a suitable amount of HCl which neutralise a part of weak base CN^- . Let concentration of $[\text{HCN}]$ be ' a ' i.e.

$$\begin{aligned} [\text{CN}^-] &= 0.01 - a \\ \text{Then} \quad \frac{[\text{CN}^-]}{[\text{HCN}]} &= \frac{0.01 - a}{a} = 0.1294 \\ \text{or} \quad a &= 9.87 \times 10^{-3} \text{ M} \\ \text{Thus} \quad [\text{HCN}] &= 9.87 \times 10^{-3} \text{ M} \\ \text{and} \quad [\text{CN}^-] &= 0.01 - 9.87 \times 10^{-3} \text{ M} \\ &= 1.277 \times 10^{-4} \text{ M} \end{aligned}$$

Thus buffer can be prepared by mixing 0.01 mole of NaCN and $9.87 \times 10^{-3} \text{ M}$ HCl in one litre of water.

SOLVED PROBLEM 17. Freshly prepared Aluminium and magnesium hydroxides are stirred vigorously in a buffer solution containing $0.25 \text{ mol lit}^{-1}$ of ammonium chloride and $0.05 \text{ mole lit}^{-1}$ of ammonium hydroxide. Calculate the concentration of Al^{3+} and Mg^{2+} ions in the solution.

$$\begin{aligned} K_b(\text{NH}_4\text{OH}) &= 1.8 \times 10^{-5} \\ K_{sp} \text{Mg}(\text{OH})_2 &= 6.0 \times 10^{-10} \\ K_{sp} \text{Al}(\text{OH})_3 &= 6.0 \times 10^{-32} \end{aligned}$$

SOLUTION : (i) To calculate pOH value

Formula used

$$pOH = pK_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

Quantities given

$$pK_b = -\log(1.8 \times 10^{-5}) = 4.7447$$

$$[\text{Salt}] = 0.25 \text{ M}$$

$$[\text{Base}] = 0.05 \text{ M}$$

Substitution of values

$$\begin{aligned} pOH &= 4.7447 + \log \frac{0.25}{0.05} \\ &= 4.7447 + \log 5 \\ &= 4.7447 + 0.6990 \\ &= 5.4437 \end{aligned}$$

(ii) To calculate the concentration of OH^- ions.

$$\begin{aligned} pOH &= -\log [\text{OH}^-] \\ 5.4437 &= -\log [\text{OH}^-] \\ [\text{OH}^-] &= \text{Antilog}(-5.4437) \\ &= 3.6 \times 10^{-6} \end{aligned}$$

(iii) To calculate the concentration of Al^{3+} and Mg^{2+} ions.

$$\begin{aligned}
 Al(OH)_3 &\rightleftharpoons Al^{3+} + 3OH^- \\
 K_{sp}[Al(OH)_3] &= [Al^{3+}][OH^-]^3 = 6.0 \times 10^{-32} \\
 \text{or} \quad [Al^{3+}] &= \frac{K_{sp}[Al(OH)_3]}{[OH^-]^3} = \frac{6.0 \times 10^{-32}}{(3.6 \times 10^{-6})^3} \\
 &= 1.286 \times 10^{-15} \text{ M} \\
 \text{Also} \quad K_{sp}[Mg(OH)_2] &= [Mg^{2+}][OH^-]^2 = 6.0 \times 10^{-10} \\
 \text{or} \quad [Mg^{2+}] &= \frac{K_{sp}[Mg(OH)_2]}{[OH^-]^2} \\
 &= \frac{6.0 \times 10^{-10}}{(3.6 \times 10^{-6})^2} \\
 &= 4.63 \times 10^{-9} \\
 &= 46.3
 \end{aligned}$$

SOLVED PROBLEM 18. What is the pH of 1.0 M solution of acetic acid? To what volume must one litre of this solution be diluted so that the pH of the resulting solution will be twice the original value? (Given $K_a = 1.8 \times 10^{-5}$)

SOLUTION : (i) To calculate the pH of 1.0 M solution of acetic acid

$$\begin{aligned}
 CH_3COOH &\rightleftharpoons CH_3COO^- + H^+ \\
 K_a &= \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \\
 &= \frac{[H^+]^2}{[CH_3COOH]} \quad \because [CH_3COOH] = [H^+] \\
 [H^+]^2 &= K_a \times [CH_3COOH] \\
 [H^+]^2 &= 1.8 \times 10^{-5} \times 1.0 \\
 \text{or} \quad H^+ &= \sqrt{1.8 \times 10^{-5} \times 1.0} \\
 &= 4.24 \times 10^{-3} \text{ M} \\
 \text{Now} \quad pH &= -\log [H^+] \\
 &= -\log (4.24 \times 10^{-3}) \\
 &= 2.3726
 \end{aligned}$$

(ii) To calculate the volume of the solution

$$\begin{aligned}
 pH \text{ of the diluted solution} &= 2 \times 2.3726 \\
 &= 4.7452 \\
 pH = -\log [H^+] &= 4.7452 = -\log \sqrt{K'_a} \\
 \text{or} \quad -1/2 \log K'_a &= 4.7452 \\
 \text{or} \quad \log K'_a &= -9.4904 \\
 \text{or} \quad K'_a &= \text{Antilog}(-9.4904) \\
 &= 3.233 \times 10^{-10} \\
 \text{Concentration of diluted } CH_3COOH &= \frac{K'_a}{K_a} \\
 [CH_3COOH]_{Dil.} &= \frac{3.233 \times 10^{-10}}{1.8 \times 10^{-5}} = 1.7961 \times 10^{-5} \text{ M}
 \end{aligned}$$

Let V be the volume of the diluted solution.

$$\begin{aligned} \text{Applying} \quad M_1 V_1 &= M_2 V_2 \\ 1 \times 1 &= 1.7961 \times 10^{-5} \times V \\ \text{or} \quad V &= \frac{1}{1.7961 \times 10^{-5}} \text{ lit} \\ &= 5.567 \times 10^4 \text{ lit} \end{aligned}$$

SOLVED PROBLEM 20. Calculate the amount of NH_3 and NH_4Cl required to prepare a buffer solution of pH 9.0 when total concentration of buffering reagent is 0.6 mol lit^{-1} . ($\text{p}K_b$ for $\text{NH}_3 = 4.7$) Also take $\log 2 = 0.3$.

SOLUTION :

Formula used

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

Quantities given

$$\text{pOH} = 14 - \text{pH} = 14 - 9.0 = 5.0$$

$$\text{p}K_b = 4.7$$

Substitution of values

$$5 = 4.7 + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$\begin{aligned} \text{or} \quad \log \frac{[\text{Salt}]}{[\text{Base}]} &= 0.3 \\ &= \log 2 \end{aligned}$$

$$\text{or} \quad \frac{[\text{Salt}]}{[\text{Base}]} = 2$$

Let the amount of NH_4Cl be $x \text{ mol lit}^{-1}$. Then

$$\frac{x}{0.6 - x} = 2$$

$$\text{or} \quad x = 1.2 - 2x$$

$$\begin{aligned} \text{or} \quad 3x &= 1.2 \\ &= 0.4 \text{ mol lit}^{-1} \end{aligned}$$

$$\text{Thus} \quad \text{the amount of } \text{NH}_4\text{Cl} = 0.4 \text{ mol lit}^{-1}$$

$$\text{and} \quad \text{the amount of } \text{NH}_3 = 0.6 - 0.4 = 0.2 \text{ mol lit}^{-1}$$

ADDITIONAL PRACTICE PROBLEMS

1. The dissociation constant of a base at 25 °C is 1.5×10^{-10} . Calculate the concentration of hydroxyl ions in 0.015 M solution. Also calculate its degree of dissociation.

Answer. 1.5×10^{-6} ; 0.0001

2. Calculate the pH of the following solution :

(i) 0.0002 M HCl

(ii) 0.1 M NH_4OH ($K_b = 1.8 \times 10^{-5}$)

Answer. (i) 3.6990 ; (ii) 11.13

3. Calculate the hydrogen ion concentration in a sample of blood having $pH = 7.4$.

Answer. $3.98 \times 10^{-8} M$

4. The concentration of HCN and NaCN in a solution is 0.01 M each. Calculate the concentration of hydrogen and hydroxyl ions if the dissociation constant of HCN is 7.2×10^{-10} .

Answer. $[H^+] = 7.2 \times 10^{-10} M$; $[OH^-] = 1.4 \times 10^{-5} M$

5. Calculate the change in pH of 1 litre of buffer solution containing 0.10 mole of each NH_3 and NH_4Cl upon addition of

(i) 0.02 mole of dissolved gaseous HCl

(ii) 0.02 mole of dissolved NaOH.

Assuming no change in solution volume K_b of $NH_3 = 1.8 \times 10^{-5}$

Answer. (i) 0.176 unit decrease (ii) 0.176 unit increase

6. A 40.0 ml solution of a weak base, B OH, is treated with 0.1 N HCl solution. The pH values of the solution are found to be 10.04 and 9.14 after the addition of 5.0 ml and 20.0 ml of the acid respectively. Find out the dissociation constant of the base.

Answer. 1.82×10^{-5}

7. What is the pH of 0.50 M aqueous NaCN solution ? pK_b of CN^- is 4.70

Answer. 11.5

8. An aqueous solution of aniline of concentration 0.24 M is prepared. What concentration of sodium hydroxide is needed in this solution so that anilinium ion concentration remains at 1×10^{-8} M ?

$$(K_a \text{ for } \text{C}_6\text{H}_5\text{NH}_3^+ = 2.4 \times 10^{-5})$$

Answer. 1×10^{-2}

9. K_a for ascorbic acid (H Asc) is 5×10^{-5} . Calculate the hydrogen ion concentration in an aqueous solution in which the concentration of Asc^- ions is 0.20 M.

Answer. 5×10^{-9} M

10. Calculate the pH of a solution made by mixing 50 ml of 0.01 M $\text{Ba}(\text{OH})_2$ solution with 50 ml of water.

Answer. 12

28

Salt Hydrolysis

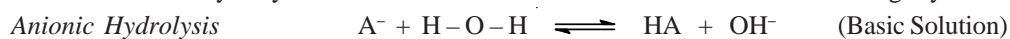
CHAPTER

KEY CONCEPTS AND EQUATIONS



HYDROLYSIS

The reaction of anion or cation with water accompanied by cleavage of O – H bond is called hydrolysis. In anionic hydrolysis the solution becomes slightly basic due to the generation of excess OH^- ions. In cationic hydrolysis there is excess of H^+ ions which make the solution slightly acidic.



Different salts on hydrolysis give acidic, basic or neutral solution depending upon their nature. Their hydrolysis behavior is summarised in Table 28.1.

TABLE 28.1 HYDROLYTIC BEHAVIOUR OF DIFFERENT TYPE OF SALTS		
Type of Salt	Examples	Resulting solution
Salt of weak acid & strong base	CH_3COOH , NaCN , etc.	Basic
Salt of weak base & strong acid	NH_4Cl , AlCl_3 , FeCl_3 , CuSO_4	Acidic
Salt of weak acid & weak base	$\text{NH}_4\text{OOCCH}_3$, NH_4CN , NH_4F	Basic or Acidic or neutral
Salt of strong acid & strong base	NaCl , KNO_3 , Na_2SO_4 , etc.	Neutral

HYDROLYSIS CONSTANT

The hydrolysis constant, K_h , of salt of a weak acid and strong base is given by

$$K_h = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

RELATION BETWEEN K_h , K_w AND K_a

$$\frac{K_w}{K_a} = K_h$$

From the relation it is clear that weaker the acid greater is the hydrolysis constant of the salt.

RELATION BETWEEN HYDROLYSIS CONSTANT AND DEGREE OF HYDROLYSIS

The degree of hydrolysis is the fraction of the salt which has undergone hydrolysis when equilibrium is established. It is represented by α and is given by

$$\alpha = \sqrt{\frac{K_w}{K_a C}}$$

To calculate pH value of an aqueous solution of weak acid and strong base.

The formula used is

$$pH = \frac{1}{2} p K_w + \frac{1}{2} p K_a + \frac{1}{2} \log C$$

Salt of weak base and strong acid

The hydrolysis constant of a salt of weak base and strong acid is given by

$$K_h = \frac{[H^+][BOH]}{[B^+]}$$

Relation between K_h , K_w and K_b

$$\frac{K_w}{K_b} = K_h$$

The hydrolysis constant K_h varies inversely as the dissociation constant, K_b , of the base.

Relation between hydrolysis constant and degree of hydrolysis

$$\alpha = \sqrt{\frac{K_w}{K_h \times C}}$$

The pH is given by

$$pH = \frac{1}{2} p K_w - \frac{1}{2} \log C + \frac{1}{2} p K_b$$

The value of pH will always be less than 7. Thus the solution of a salt of weak base and strong acid will always be acidic.

Salt of weak acid and weak base

The hydrolysis constant is given by

$$K_h = \frac{K_w}{K_a \times K_b}$$

and the degree of hydrolysis is given by

$$\alpha = \sqrt{\frac{K_w}{K_a \times K_b}}$$

The pH of the solution is given by

$$pH = \frac{1}{2} p K_w + \frac{1}{2} p K_a - \frac{1}{2} p K_b$$

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. Calculate the pH of 0.05 N sodium benzoate solution. K_a for $C_6H_5COOH = 6.37 \times 10^{-5}$ and $K_w = 1 \times 10^{-14}$

SOLUTION :

Formula used

$$pH = \frac{1}{2} p K_w + \frac{1}{2} p K_a + \frac{1}{2} \log C$$

Quantities given

$$pK_w = -\log 10^{-14} = 14$$

$$C = 0.05$$

$$pK_a = -\log 6.37 \times 10^{-5} = 4.1958$$

Substitution of values

$$\begin{aligned} pH &= \frac{1}{2} \times 14 + \frac{1}{2} \times 4.1958 + \frac{1}{2} (1.3010) \\ &= 7 + 2.0979 - 0.6505 \\ &= \mathbf{8.4474} \end{aligned}$$

SOLVED PROBLEM 2. Sodium phenate is hydrolysed to the extent of 0.03% in 0.1 M aqueous solution at 25 °C. Calculate the (i) hydrolysis constant of the salt and (ii) the ionic product of water at 25 °C. The dissociation constant of phenol is 1.3×10^{-10} at 25 °C.

SOLUTION : (i) To calculate the ionic product of water

Formula used

$$\alpha = \sqrt{\frac{K_w}{K_a \times C}}$$

Quantities given

$$\alpha = 0.03$$

$$K_a = 1.3 \times 10^{-10}$$

$$C = 0.1$$

Substitution of values

$$\begin{aligned} \frac{K_w}{K_a \times C} &= \alpha^2 \\ K_w &= 1.3 \times 10^{-10} \times 0.1 \times (0.03)^2 \\ &= \mathbf{1.17 \times 10^{-14}} \end{aligned}$$

(ii) To calculate the hydrolysis constant

Formula used

$$K_h = \frac{K_w}{K_a}$$

Quantities given

$$K_w = 1.17 \times 10^{-14}$$

$$K_a = 1.3 \times 10^{-5}$$

Substitution of values

$$\begin{aligned} K_h &= \frac{1.17 \times 10^{-14}}{1.3 \times 10^{-5}} \\ &= 0.9 \times 10^{-9} \\ &= \mathbf{9 \times 10^{-10}} \end{aligned}$$

SOLVED PROBLEM 3. A 0.02 M solution of sodium acetate in water at 25 °C has a hydrogen concentration of 3×10^{-9} M. What is the hydrolysis constant of the salt ?

SOLUTION : (i) To calculate the K_a of the acid

Formula used

$$[H^+] = \sqrt{\frac{K_w K_a}{C}} \quad \text{or} \quad [H^+]^2 = \frac{K_w K_a}{C}$$

Quantities given

$$[H^+] = 3 \times 10^{-9}$$

$$K_w = 1 \times 10^{-14}$$

$$C = 0.02$$

Substitution of values

$$(3 \times 10^{-9})^2 = \frac{10^{-14} \times K_a}{0.02}$$

or

$$K_a = \frac{9 \times 10^{-18} \times 0.02}{10^{-14}} = 1.8 \times 10^{-5}$$

(ii) To calculate the hydrolysis constant of sodium acetate.

Formula used

$$K_h = \frac{K_w}{K_a}$$

Quantities given

$$K_w = 10^{-14}$$

$$K_a = 1.8 \times 10^{-5}$$

Substitution of values

$$\begin{aligned} K_h &= \frac{10^{-14}}{1.8 \times 10^{-5}} \\ &= 5.5 \times 10^{-10} \end{aligned}$$

SOLVED PROBLEM 4. Calculate the pH of a decinormal solution of ammonium chloride.

($pK_a = 5.7$ and $pK_b = 14$).

SOLUTION :

Formula used

$$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_b - \frac{1}{2} \log C$$

Quantities given

$$pK_b = 5.7$$

$$pK_w = 14$$

Substitution of values

$$\begin{aligned} pH &= 7 + \frac{1}{2} \times 5.7 - \frac{1}{2} \log 0.1 \\ &= 7 + 2.85 - \frac{1}{2} (-1) \\ &= 7 + 2.85 + 0.5 \\ &= 10.35 \end{aligned}$$

SOLVED PROBLEM 5. The dissociation constant of acetic acid is 1.8×10^{-5} at 18°C . The ionic product of water is 10^{-14} at 18°C . What would be the degree of hydrolysis in a 0.012 N solution of sodium acetate?

SOLUTION :

Formula used

$$\alpha = \sqrt{\frac{K_w}{K_a \times C}}$$

Quantities given

$$K_w = 10^{-14}$$

$$K_a = 1.8 \times 10^{-5}$$

$$C = 0.012$$

Substitution of values

$$\begin{aligned} \alpha &= \sqrt{\frac{10^{-14}}{1.8 \times 10^{-5} \times 0.012}} \\ &= \sqrt{4.623 \times 10^{-9}} \\ &= 6.799 \times 10^{-5} \end{aligned}$$

SOLVED PROBLEM 6. Calculate the degree of hydrolysis of sodium acetate. Dissociation constant of acetic acid is 1.8×10^{-5} and Ionic product of water is 1×10^{-14}

SOLUTION :

Formula used

$$\alpha = \sqrt{\frac{K_w}{K_a \times C}}$$

Quantities given

$$K_w = 1 \times 10^{-14}$$

$$K_a = 1.80 \times 10^{-5} \quad C = 0.1$$

Substitution of values

$$\begin{aligned} \alpha &= \sqrt{\frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5} \times 0.1}} \\ &= \sqrt{5.55 \times 10^{-9}} \\ &= 7.45 \times 10^{-5} \end{aligned}$$

SOLVED PROBLEM 7. Calculate the percentage of hydrolysis of sodium acetate in 0.1 N solution at 25 °C using the following data. It is to be assumed that the salt is completely dissociated.

$$K_a = 1.8 \times 10^{-5}; K_w = 1.02 \times 10^{-14}.$$

SOLUTION :**Formula used**

$$\alpha = \sqrt{\frac{K_w}{K_a \times C}}$$

Quantities given

$$K_w = 1.02 \times 10^{-14}$$

$$K_a = 1.8 \times 10^{-5} \quad C = 0.1$$

Substitution of values

$$\begin{aligned} \alpha &= \sqrt{\frac{1.02 \times 10^{-14}}{1.8 \times 10^{-5} \times 0.1}} \\ &= 7.527 \times 10^{-5} \end{aligned}$$

SOLVED PROBLEM 8. The dissociation constant of ammonium hydroxide and hydrocyanic acid are respectively 1.8×10^{-5} and 7.2×10^{-7} and the ionic product of water is 1×10^{-14} . Calculate the degree of hydrolysis and hydrolytic constant for ammonium cyanide in 0.01 M solution.

SOLUTION :**Formula used**

$$\alpha = \sqrt{\frac{K_w}{K_a \times K_b}}$$

Quantities given

$$K_w = 1 \times 10^{-14}$$

$$K_a = 1.8 \times 10^{-5} \quad K_b = 7.2 \times 10^{-7}$$

Substitution of values

$$\begin{aligned} \alpha &= \sqrt{\frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5} \times 7.2 \times 10^{-7}}} \\ &= \sqrt{7.716 \times 10^{-4}} \\ &= 2.777 \times 10^{-2} \end{aligned}$$

SOLVED PROBLEM 9. A 0.02 molar solution of sodium acetate in water at 25 °C is found to have a hydrogen ion concentration of 3.0×10^{-9} gram ion weight per litre. What is the hydrolytic constant of the salt ? ($K_w = 1 \times 10^{-14}$).

SOLUTION :**(i) To calculate the value of K_a**

Formula used

$$pH = \frac{1}{2} p K_w + \frac{1}{2} p K_a + \frac{1}{2} \log C$$

Quantities given

$$pH = -\log [H^+] = -\log (3 \times 10^{-9}) = 8.523 \quad C = 0.02M$$

Substitution of values

$$\begin{aligned} 8.523 &= 7 + \frac{1}{2} p K_a + \frac{1}{2} \log (0.02) \\ &= 7 + \frac{1}{2} p K_a + \frac{1}{2} (-1.6990) \end{aligned}$$

$$\begin{aligned} p K_a &= 2 \times (8.523 - 7 + 0.8495) \\ &= 4.745 \end{aligned}$$

or

$$\begin{aligned} K_a &= \text{Antilog} (4.745) \\ &= 1.80 \times 10^{-5} \end{aligned}$$

(ii) To calculate the hydrolysis constant

Formula used

$$K_h = \sqrt{\frac{K_w}{K_a \times C}}$$

Quantities given

$$K_w = 1 \times 10^{-14}$$

$$K_a = 1.80 \times 10^{-5}$$

$$C = 0.02$$

Substitution of values

$$\begin{aligned} K_h &= \sqrt{\frac{1 \times 10^{-14}}{1.80 \times 10^{-5} \times 0.02}} \\ &= \sqrt{2.777 \times 10^{-8}} \\ &= 1.666 \times 10^{-4} \end{aligned}$$

SOLVED PROBLEM 10. Calculate the hydrolysis constant, degree of hydrolysis and pH value of $10^{-2} M NH_4Cl$ solution at 290 K. ($K_b = 1.8 \times 10^{-5}$ and $K_w = 1.0 \times 10^{-14}$).

SOLUTION : (i) To calculate the hydrolysis constant

Formula used

$$K_h = \frac{K_w}{K_b}$$

Quantities given

$$K_w = 1.0 \times 10^{-14}$$

$$K_b = 1.8 \times 10^{-5}$$

Substitution of values

$$\begin{aligned} K_h &= \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} \\ &= 5.55 \times 10^{-10} \end{aligned}$$

(ii) To calculate the degree of hydrolysis

Formula used

$$\alpha = \sqrt{\frac{K_w}{K_b \times C}}$$

Quantities given

$$K_w = 1 \times 10^{-14}$$

Substitution of values

$$K_b = 1.8 \times 10^{-5}$$

$$C = 10^{-2}$$

$$\begin{aligned}\alpha &= \sqrt{\frac{1 \times 10^{-14}}{1.8 \times 10^{-5} \times 10^{-2}}} \\ &= \sqrt{5.555 \times 10^{-8}} \\ &= 2.357 \times 10^{-4}\end{aligned}$$

(iii) To calculate the pH**Quantities given**

$$pK_w = 14$$

Substitution of values

$$pH = \frac{1}{2} pK_w - \frac{1}{2} pK_b + \frac{1}{2} \log C$$

$$pK_b = -\log 1.8 \times 10^{-5} = 4.7447 \quad C = 10^{-2}$$

$$\begin{aligned}pH &= \frac{1}{2} \times 14 - \frac{1}{2} (4.7447) + \frac{1}{2} \log 10^{-2} \\ &= 7 - 2.37235 + \frac{1}{2} (-2) \\ &= 3.62765\end{aligned}$$

SOLVED PROBLEM 11. The hydrogen ion concentration of 0.02 sodium acetate is found to be 3.0×10^{-9} M at 25 °C. Calculate the hydrolysis constant of this salt. $K_w = 1.0 \times 10^{-14}$.

SOLUTION : (i) To calculate K_a of the acid**Formula used**

$$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a + \frac{1}{2} \log C$$

Quantities given

$$pH = -\log (3.0 \times 10^{-9}) = 8.523$$

Substitution of values

$$pK_w = -\log (1 \times 10^{-14}) = 14 \quad C = 0.02\text{M} = 10^{-2}\text{M}$$

$$8.523 = \frac{1}{2} \times 14 + \frac{1}{2} pK_a + \frac{1}{2} \log 10^{-2}$$

$$8.523 = 7 + \frac{1}{2} pK_a + \frac{1}{2} (-1.6989)$$

or

$$\begin{aligned}pK_a &= 2 \times (1.523 + 0.84945) \\ &= 4.7449\end{aligned}$$

or

$$K_a = \text{Antilog} (-4.7449) = 1.799 \times 10^{-5}$$

(ii) To calculate the hydrolysis constant**Formula used**

$$K_h = \frac{K_w}{K_a}$$

Quantities given

$$K_w = 1.0 \times 10^{-14}$$

Substitution of values

$$K_a = 1.799 \times 10^{-5}$$

$$\begin{aligned}K_h &= \frac{1 \times 10^{-14}}{1.799 \times 10^{-5}} \\ &= 5.55 \times 10^{-10}\end{aligned}$$

SOLVED PROBLEM 12. Calculate the hydrolysis constant and degree of hydrolysis of 0.1M sodium acetate solution. Given : $K_w = 1.0 \times 10^{-14}$ and $K_a = 1.75 \times 10^{-5}$

SOLUTION : (i) To calculate hydrolysis constant

Formula used

$$K_h = \frac{K_w}{K_a}$$

Quantities given

$$K_w = 1.0 \times 10^{-14}$$

$$K_a = 1.75 \times 10^{-5}$$

Substitution of values

$$\begin{aligned} K_h &= \frac{1.0 \times 10^{-14}}{1.75 \times 10^{-5}} \\ &= 5.71 \times 10^{-10} \end{aligned}$$

(ii) To calculate the hydrolysis constant

Formula used

$$\alpha = \sqrt{\frac{K_h}{C}}$$

Quantities given

$$K_h = 5.71 \times 10^{-10}$$

$$C = 0.1$$

Substitution of values

$$\begin{aligned} \alpha &= \sqrt{\frac{5.71 \times 10^{-10}}{0.1}} \\ &= 7.55 \times 10^{-5} \end{aligned}$$

SOLVED PROBLEM 13. Calculate the percentage hydrolysis of sodium acetate in 0.2 M solution at 25 °C assuming the salt is completely dissociated. K_a for acetic acid = 1.8×10^{-5} and $K_w = 1.0 \times 10^{-14}$.

SOLUTION :

Formula used

$$\alpha = \sqrt{\frac{K_w}{K_a \times C}}$$

Quantities given

$$K_w = 1.0 \times 10^{-14}$$

$$K_a = 1.8 \times 10^{-5}$$

$$C = 0.2 \text{ M}$$

Substitution of values

$$\begin{aligned} \alpha &= \sqrt{\frac{1 \times 10^{-14}}{1.8 \times 10^{-5} \times 0.2}} \\ &= \sqrt{2.777 \times 10^{-9}} \\ &= 5.27 \times 10^{-5} \\ \% \text{ Hydrolysis} &= 5.27 \times 10^{-5} \times 100 \\ &= 5.27 \times 10^{-3} \% \end{aligned}$$

SOLVED PROBLEM 14. Calculate the pH at the equivalence point when a solution of 0.10M acid is titrated with a solution of 0.10 M sodium hydroxide. K_a for acetic acid = 1.9×10^{-5} .

SOLUTION :**Formula used**

$$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a + \frac{1}{2} \log C$$

Quantities given

$$pK_w = 14 \quad pK_a = -\log K_a = \log (1.9 \times 10^{-5}) = 4.7212 \quad C = \frac{0.1 \text{ M}}{2} = 0.05 \text{ M}$$

Substitution of values

$$\begin{aligned} pH &= \frac{1}{2} \times 14 + \frac{1}{2} \times 4.7212 + \frac{1}{2} \log 0.05 \\ &= 7 + 2.3606 - \frac{1.3010}{2} \\ &= \mathbf{8.7101} \end{aligned}$$

SOLVED PROBLEM 15. Calculate the pH and hydrolysis constant of 0.05 M NH_4Cl solution.

$$K_{\text{NH}_4\text{OH}} = 1.75 \times 10^{-5} \quad \text{and} \quad K_w = 1 \times 10^{-14}.$$

SOLUTION : (i) To calculate pH value**Formula used**

$$pH = \frac{1}{2} pK_w - \frac{1}{2} pK_b - \frac{1}{2} \log C$$

Quantities given

$$pK_w = -\log K_w = -\log 1 \times 10^{-14} = 14 \quad pK_b = -\log K_b = -\log 1.75 \quad C = 0.05 \text{ M}$$

Substitution of values

$$\begin{aligned} pH &= \frac{1}{2} \times 14 - \frac{1}{2} \times (4.7569) - \frac{1}{2} \log 0.05 \\ &= 7 - 2.37845 - (-1.3010) \\ &= \mathbf{5.92255} \end{aligned}$$

(ii) To calculate the hydrolysis constant**Formula used**

$$K_h = \frac{K_w}{K_b}$$

Quantities given

$$K_w = 1 \times 10^{-14} \quad K_b = 1.75 \times 10^{-5}$$

Substitution of values

$$\begin{aligned} K_h &= \frac{1 \times 10^{-14}}{1.75 \times 10^{-5}} \\ &= \mathbf{5.714 \times 10^{-10}} \end{aligned}$$

SOLVED PROBLEM 16. Calculate the degree of hydrolysis and pH of 0.02M solution of sodium acetate. Hydrolysis constant of sodium acetate is 5.6×10^{-10} .**SOLUTION : (i) To calculate the degree of hydrolysis****Formula used**

$$K_a = \sqrt{\frac{K_h}{C}}$$

Quantities given

$$K_h = 5.6 \times 10^{-10}$$

$$C = 0.02\text{M}$$

Substitution of values

$$\begin{aligned}\alpha &= \sqrt{\frac{5.6 \times 10^{-10}}{0.02}} \\ &= \sqrt{2.8 \times 10^{-8}} \\ &= 1.67 \times 10^{-4}\end{aligned}$$

(ii) To calculate the pH of the solution**Formula used**

$$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a + \frac{1}{2} \log C$$

Quantities given

$$pK_w = 14$$

$$C = 0.02\text{ M}$$

$$\begin{aligned}pK_a &= -\log K_a = -\log \frac{K_w}{K_h} = -\log \frac{10^{-14}}{5.6 \times 10^{-10}} \\ &= -\log 1.786 \times 10^{-5} = +4.7482\end{aligned}$$

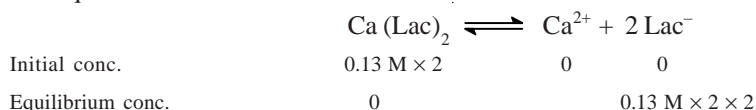
Substitution of values

$$\begin{aligned}pH &= \frac{1}{2} \times 14 + \frac{1}{2} (+4.7482) + \frac{1}{2} \log (0.02) \\ &= 7 + 2.3741 + \frac{1}{2} (-1.6990) \\ &= 9.3741 - 0.8495 \\ &= 8.5246\end{aligned}$$

SOLVED PROBLEM 17. Calcium lactate is a salt of a weak organic acid and represented by $\text{Ca}(\text{Lac})_2$. A saturated solution of $\text{Ca}(\text{Lac})_2$ contain 0.13 mol of this salt in 0.5 litre solution. The pOH of this solution is 5.60. Assuming complete dissociation of the salt, calculate K_a of Lactic acid.

SOLUTION :

The equilibrium reaction is

**Formula used**

$$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a + \frac{1}{2} \log C$$

Quantities given

$$pK_w = 14$$

Substitution of values

$$pH = pK_w - pOH = 14 - 5.60 = 8.4 \quad C = 0.52\text{ M}$$

$$\begin{aligned}8.40 &= \frac{1}{2} \times 14 + \frac{1}{2} pK_a + \frac{1}{2} \log 0.52 \\ &= 7 + \frac{1}{2} pK_a + \frac{1}{2} (-0.2840) \\ \frac{1}{2} pK_a &= 8.40 - 7 + 0.142 \\ pK_a &= 2 \times 1.542 = 3.084 \\ K_a &= \text{Antilog}(-3.084) \\ &= 8.24 \times 10^{-4}\end{aligned}$$

or

SOLVED PROBLEM 18. Calculate the pH of 0.50 M aqueous NaCN solution. pK_b of CN^- is 4.70.

SOLUTION :

Formula used

$$pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a + \frac{1}{2} \log C$$

Quantities given

$$pK_w = 14$$

$$pK_a = 14 - pK_b = 14 - 4.70 = 9.30$$

$$C = 0.50 \text{ M}$$

Substitution of values

$$\begin{aligned} pH &= \frac{1}{2} \times 14 + \frac{1}{2} \times 9.30 + \frac{1}{2} \log 0.50 \\ &= 7 + 4.65 + \frac{1}{2} (-0.3010) \\ &= 11.65 - 0.1505 \\ &= \mathbf{11.4995} \end{aligned}$$

SOLVED PROBLEM 19. Calculate the percentage of hydrolysis of 0.003 M aqueous solution of NaOCN.

$$K_a \text{ for HOCN} = 3.33 \times 10^{-4}$$

SOLUTION :

Formula used

$$\alpha = \sqrt{\frac{K_w}{K_a \times C}}$$

Quantities given

$$K_w = 1 \times 10^{-14}$$

$$K_a = 3.33 \times 10^{-4}$$

$$C = 0.003 \text{ M}$$

Substitution of values

$$\begin{aligned} \alpha &= \sqrt{\frac{1 \times 10^{-14}}{3.33 \times 10^{-4} \times 0.003}} \\ &= \sqrt{1.0 \times 10^{-8}} \\ &= 1.0 \times 10^{-4} \\ \% \text{ age of hydrolysis} &= 1.0 \times 10^{-4} \times 100 \\ &= \mathbf{1.0 \times 10^{-2}} \end{aligned}$$

SOLVED PROBLEM 20. K_a for ascorbic acid (HAsc) is 5×10^{-5} . Calculate the hydrogen ion concentration and percentage of hydrolysis in aqueous solution in which the concentration of Asc^- ions is 0.02 M.

SOLUTION : The equilibrium reaction is

	$Asc^- + H_2O$	$HAsc + OH^-$
Initial Conc.	0.02	0 0
Equilibrium Conc.	$0.02 - x$	x x

(i) To calculate the concentration of H^+ .

Formula used

$$K_h = \frac{[HAsc][OH^-]}{[Asc^-]} = \frac{x^2}{0.02 - x}$$

Quantities given

$$K_h = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{5 \times 10^{-5}} = 2 \times 10^{-10}$$

Substitution of values

$$2 \times 10^{-10} = \frac{x^2}{0.02} \quad (\text{neglecting } x \text{ in denominator})$$

$$x^2 = 2 \times 10^{-10} \times 0.02$$

or

$$x = \sqrt{4 \times 10^{-12}}$$

$$= 2 \times 10^{-6}$$

$$[OH^-] = 2 \times 10^{-6}$$

and

$$[H^+] = \frac{K_w}{2 \times 10^{-6}} = \frac{1 \times 10^{-14}}{2 \times 10^{-6}} = 5 \times 10^{-9} \text{ M}$$

(ii) To calculate the degree of hydrolysis

$$\begin{aligned} \text{Percentage of hydrolysis} &= \frac{2 \times 10^{-6}}{0.02} \times 100 \\ &= 0.01\% \end{aligned}$$

ADDITIONAL PRACTICE PROBLEMS

- 20 ml of 0.1 M NaOH solution is added to 100 ml of 0.1 M solution of acetic acid calculate the pH of the buffer solution (K_a for $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$)
Answer. 4.423
- How many moles of sodium propionate should be added to the litre of an aqueous solution containing 0.02 mole of propionic acid to obtain a buffer of $pH = 4.75$? What will be the pH if 0.01 mole of HCl is added ?
Answer. $1.52 \times 10^{-2} \text{ M}$; 4.11
- 20 ml of 0.2 M NaOH solution be treated with 40 ml of 0.2 M acetic acid solution to give 70 ml. Calculate the pH of the solution.
Answer. 4.5684
- The pH of 0.1 M HCN solution is 5.2. Calculate the value of K_a for HCN.
Answer. 39.7×10^{-11}
- How many gram mole of Cl will be required to prepare one litre of a buffer solution of NaCN and HCN of pH 8.5 using 0.01 gm formula weight of NaCN ?
Answer. 0.0089 M
- What happens to the pH of 500 ml of solution that is 0.1 molar in sodium acetate and 0.1 molar in acetic acid when 10 ml of 0.1 M NaOH is added ?
Answer. pH will increase
- Calculate the percent hydrolysis of 0.1 M hydrazine hydrochloride if the basic ionization constant for hydrazine ($\text{NH}_2 - \text{NH}_2$) is 9.6×10^{-7} .
Answer. 0.032%

8. Calculate the pH at the equivalence point when a solution of 0.10 M acetic acid is titrated with a solution of 0.10 M NaOH. K_a for acetic acid is 1.9×10^{-5} .
Answer. 8.71
9. Calculate the hydrolysis constant of sodium acetate and degree of hydrolysis in 0.001M solution. Also calculate its pH value. Given K_a for acetic acid = 1.75×10^{-5} and K_w for water = 1×10^{-14} .
Answer. 5.7×10^{-10} ; 7.55×10^{-4} ; 7.88
10. Calculate the hydrolysis of KF. Determine the degree of hydrolysis of salt in 0.01 M solution. Also calculate the pH of the solution. K_a (HF) = 1.6×10^{-4} .
Answer. 1.5×10^{-11} ; 3.87×10^{-5} ; 7.59
11. The pH of a 0.1 M solution of NH_4Cl is 5.127. Calculate the degree of hydrolysis and hydrolysis constant of NH_4Cl .
Answer. 7.46×10^{-5} ; 5.56×10^{-10}
12. Calculate the percentage hydrolysis of sodium acetate in 0.1 N solution at 298 K, assuming the salt to be completely dissociated. (K_a for Acetic acid = 1.8×10^{-5})
Answer. 0.0075%
13. Calculate the degree of hydrolysis of potassium acetate in 0.1 M solution. Also calculate the pH of the solution if K_a for CH_3COOH is 1.8×10^{-5} .
Answer. 7.5×10^{-5} ; 8.88
14. Calculate the degree of hydrolysis of a mixture of aniline and acetic acid in 0.1 M solution.
($K_a = 1.8 \times 10^{-5}$ and $K_b = 4.6 \times 10^{-10}$)
Answer. 0.523
15. The concentration of H^+ ions in a 0.2 M solution of $HCOOH$ is 6.4×10^{-3} mole lit^{-1} . To this solution sodium formate is added so as to adjust the concentration of sodium formate to be 1 mole lit^{-1} . Calculate the pH of the solution. K_a for $HCOOH$ = 2.4×10^{-4} and degree of dissociation of $HCOONa$ is 74%.
Answer. 4.18

29

Electromotive Force

CHAPTER

KEY CONCEPTS AND EQUATIONS



REDOX REACTION

A reaction in which loss of electrons (oxidation) and gain of electrons take place simultaneously is called Oxidation-Reduction reaction or Redox reaction. The half reaction that occurs by oxidation is called oxidation half reaction and the second half that occurs by reduction is called reduction half reaction.

ELECTROCHEMICAL CELLS

A device for producing an electrical current from a chemical reaction (redox reaction) is called an electrochemical cell. It consists of two half cells joined together with the help of a salt bridge. The emf of a cell is given by

$$\begin{aligned} E_{cell} &= E_{cathode} - E_{anode} \\ &= E_R - E_L \end{aligned}$$

where E_R and E_L are the reduction potentials of right and left cells respectively.

RELATION BETWEEN EMF AND FREE ENERGY

When a cell produces a current, the currents can be used to do work. The maximum amount of work, W_{max} , obtainable from the cell by

$$W_{max} = -nFE$$

where n is the number of electrons transferred and is equal to the valence of the ion participating in the cell reaction, F stands for Faraday and is equal to 96500 coulombs and E is the EMF of the cell.

THE NERNST EQUATION

Nernst derived a mathematical relationship which enables us to calculate the half cell, E from the standard electrode potential, E° , with the help of the following relation.

$$E = E^\circ - \frac{2.303 RT}{nF} \log K$$

where K is the equilibrium constant for the half-cell reaction.

For the reaction



Nernst equation becomes

$$E = E^\circ - \frac{2.303 RT}{nF} \log \frac{[M^{n+}]}{[M]}$$

The concentration of solid metal $[M]$ is equal to zero.

Thus
$$E = E^\circ - \frac{2.303 RT}{nF} \log [M^{n+}]$$

CONCENTRATION CELL

Cell potential depends on the concentration of the electrolyte. Thus a cell can be constructed by pairing two half cells in which identical electrodes are dipping in solutions of different concentrations of the same electrolyte. Such a cell is called concentration cell.

The emf of a concentration cell is given by

$$E_{cell} = \frac{2.303 RT}{nF} \log \frac{C_2}{C_1}$$

or

$$E_{cell} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

DETERMINATION OF pH

A half cell is set up with the test solution as electrolyte. The emf of the cell depends upon the concentration of H^+ ions or pH of the solution. The emf of the half cell is determined by coupling it with another standard half-cell and measuring the emf of the complete cell. The equations obtained by using different electrodes are as follows :

(i) Using Hydrogen electrode

$$E_{cell} = 0.0591 \times pH \quad \text{or} \quad pH = \frac{E_{cell}}{0.0591}$$

(ii) Using Standard calomel

$$E_{cell} = 0.2415 + 0.0591 \times pH \quad \text{or} \quad pH = \frac{E_{cell} - 0.245}{0.0591}$$

(iii) Using Quinhydrone electrode

$$E_{cell} = 0.6996 + 0.0591 \times pH - 0.2415 \quad \text{or} \quad pH = \frac{0.4581 - E_{cell}}{0.0591}$$

ADDITIONAL SOLVED PROBLEMS

SOLVED PROBLEM 1. Calculate the emf of the following cell



SOLUTION :

Formula used

$$E_{cell} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

Quantities given

$$n = 2$$

$$C_2 = 0.5 \text{ N}$$

$$C_1 = 0.75 \text{ N}$$

Substitution of values

$$\begin{aligned} E_{cell} &= \frac{0.0591}{2} \log \frac{0.5}{0.75} \\ &= \frac{0.0591}{2} \log \frac{2}{3} \end{aligned}$$

$$= \frac{0.0591}{2} \times (-0.1760)$$

$$= -0.0052$$

SOLVED PROBLEM 2. The emf of the cell set up as under was found to be 0.1182 volt at 25 °C. Calculate the solubility of AgCl.

**SOLUTION :****Formula used**

$$E_{\text{cell}} = \frac{0.0591}{n} \log \frac{C_2}{C_1}$$

Quantities given

$$E_{\text{cell}} = 0.1182 \text{ V} \quad C_2 = 0.001 \quad n = 1$$

Substitution of values

$$0.1182 = \frac{0.0591}{n} \log \frac{0.001}{C_1}$$

$$\text{or} \quad \log \frac{0.001}{C_1} = \frac{0.1182}{0.0591}$$

$$= 2$$

$$\text{or} \quad \frac{0.001}{C_1} = \text{antilog } 2$$

$$= 100$$

$$\text{or} \quad C_1 = \frac{0.001}{100}$$

$$= 1 \times 10^{-5} \text{ g mol}^{-1}$$

$$\therefore \text{Solubility, } C_1 = 1 \times 10^{-5} \times 143.5 \text{ g lit}^{-1}$$

$$= 1.435 \times 10^{-3} \text{ g lit}^{-1}$$

SOLVED PROBLEM 3. The emf of the following cell,



was found to be 0.228 volt at 25 °C. Calculate the pH of the solution. ($E_{\text{cal}} = 0.2415 \text{ Volt}$)

SOLUTION :**Formula used**

$$\text{pH} = \frac{0.4581 - E_{\text{cell}}}{0.0591}$$

Quantities given

$$E_{\text{cell}} = 0.228 \text{ V}$$

Substitution of values

$$\text{pH} = \frac{0.4581 - 0.228}{0.0591}$$

$$= 3.89$$

SOLVED PROBLEM 4. The emf of the cell set up by using an acid solution, standard calomel electrode and quinhydrone electrode, was found to be 0.1595 volt at 25 °C. Calculate the pH of the acid solution. (emf of standard calomel electrode = -0.2440 V and emf quinhydrone electrode = -0.6990 V)

SOLUTION :

Formula used

$$E_{cell} = \left[E_{Q^+} - \frac{2.303 RT}{n} pH \right] - E_{SCE}$$

Quantities given

$$E_{Q^+} = 0.6990 \text{ V}$$

$$E_{SCE} = -0.2440$$

$$\frac{2303 RT}{F} = 0.0591$$

$$E_{cell} = 0.1595$$

Substitution of values

$$0.1595 = [0.6990 - 0.0591 pH] - 0.2440$$

$$0.1595 = 0.6990 - 0.0591 pH - 0.2440$$

$$0.1595 = 0.4550 - 0.0591 pH$$

$$\begin{aligned} \text{or} \quad pH &= \frac{0.4550 - 0.1595}{0.0591} \\ &= 5 \end{aligned}$$

SOLVED PROBLEM 5. Calculate the single electrode potential for copper metal in contact with 0.1 M Cu^{2+} solution. $E^\circ_{\text{Cu}^{2+}/\text{Cu}}$ is 0.34 volt.

SOLUTION :

Formula used

$$E = E^\circ - \frac{0.0591}{n} \log [\text{Cu}^{2+}]$$

Quantities given

$$E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \text{ V} \quad [\text{Cu}^{2+}] = 0.1 \text{ M}$$

$$n = 2$$

Substitution of values

$$\begin{aligned} E &= 0.34 \text{ V} - \frac{0.0591}{2} \log 0.1 \\ &= 0.34 \text{ V} - 0.02955 \times (-1) \\ &= 0.36955 \text{ V} \end{aligned}$$

SOLVED PROBLEM 6. Hydrogen electrode and normal calomel electrode when immersed in a solution at 25 °C showed a potential of 0.664 V. Calculate the pH of the solution.

SOLUTION :

Formula used

$$E_{cell} = 0.2415 + 0.0591 \times pH$$

Quantities given

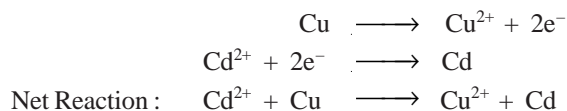
$$E_{cell} = 0.664 \text{ V}$$

Substitution of values

$$0.664 \text{ V} = 0.2415 + 0.0591 pH = \frac{0.664 - 0.2415}{0.0591} = 7.1489$$

SOLVED PROBLEM 7. What will be the reaction in the cell which is made by combining standard Cd half cell with standard Cu half cell ? Also calculate the emf of the cell. The standard oxidation potential of half cells are 0.453 and -0.337 V.

SOLUTION : The cell reactions are



Formula used

$$E_{\text{cell}} = \text{Reduction potential of cathode} - \text{Reduction potential of anode}$$

Quantities given

$$\text{Reduction potential of cathode} = -0.337 \text{ V}$$

$$\text{Reduction potential of anode} = 0.453 \text{ V}$$

Substitution of values

$$\begin{aligned} E_{\text{cell}} &= -0.337 \text{ V} - 0.453 \text{ V} \\ &= -0.790 \text{ V} \end{aligned}$$

SOLVED PROBLEM 8. Calculate the emf of the cell :



$$\text{Given } E_{\text{Ag/Ag}^+}^{\circ} = 0.799 \text{ V}$$

$$E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = 0.763 \text{ V}$$

Is the reaction spontaneous ?

SOLUTION :

Formula used

$$\text{EMF of the cell} = E_R - E_L$$

Quantities given

$$E_R = -0.763 \text{ V}$$

$$E_L = 0.799 \text{ V}$$

Substitution of values

$$\begin{aligned} \text{EMF of the cell} &= -0.763 \text{ V} - (0.799 \text{ V}) \\ &= -1.562 \text{ V} \end{aligned}$$

Since the emf of the cell is negative, the reaction is not spontaneous.

SOLVED PROBLEM 9. Calculate the free energy change of the following cell at 25°C .



The standard emf of the cell is 0.14 V.

SOLUTION :

Formula used

$$\Delta G = -nFE$$

Quantities given

$$n = 2$$

$$F = 96500$$

$$E = 0.14 \text{ V}$$

Substitution of values

$$\begin{aligned} \Delta G &= 2 \times 96500 \times 0.14 \text{ J} \\ &= 27020 \text{ J} \end{aligned}$$

SOLVED PROBLEM 10. When hydrogen electrode and normal calomel electrode are immersed in a solution at 25 °C, a potential of 0.624 is obtained. Calculate the *pH* of the solution.

SOLUTION :

Formula used

$$pH = \frac{E_{cell} - 0.2415}{0.0591}$$

Quantities given

$$E_{cell} = 0.624 \text{ V}$$

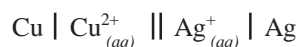
Substitution of values

$$\begin{aligned} pH &= \frac{0.624 - 0.2415}{0.0591} \\ &= \mathbf{6.47} \end{aligned}$$

SOLVED PROBLEM 11. The standard reduction potential of Cu^{2+}/Cu and Ag^+/Ag electrodes are 0.337 and 0.799 volt respectively. Construct a galvanic cell using these electrodes so that its standard emf is positive. For what concentration of Ag^+ will the emf of solution at 25 °C be zero if the concentration of Cu^{2+} is 0.01 M ?

SOLUTION : (i) To calculate the emf of the cell

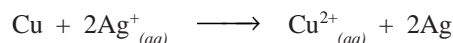
The cell would be



and the cell reactions are



The net cell reaction is



EMF of the cell is

$$\begin{aligned} EMF &= E^\circ_{\text{Right}} - E^\circ_{\text{Left}} \\ &= 0.799 \text{ V} - 0.337 \text{ V} \\ &= \mathbf{0.462 \text{ V}} \end{aligned}$$

(ii) To calculate the concentration of Cu^{2+} ions

Formula used

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{[\text{Cu}^{2+}]}{[\text{Ag}^+]^2}$$

Quantities given

$$E_{cell} = 0 \quad n = 2 \quad [\text{Cu}^{2+}] = 0.01 \text{ M} \quad E^\circ_{cell} = 0.462 \text{ V}$$

Substitution of values

$$0 = 0.462 \text{ V} - \frac{0.0591}{2} \log \frac{0.01}{[\text{Ag}^+]^2}$$

$$\begin{aligned} \text{or} \quad \log \frac{0.01}{[\text{Ag}^+]^2} &= \frac{2 \times 0.462}{0.0591} \\ &= 14.9577 \end{aligned}$$

$$\begin{aligned}
 \text{or} \quad \frac{0.01}{[\text{Ag}^+]^2} &= \text{Antilog } 14.9577 \\
 &= 9.072 \times 10^{14} \\
 \text{or} \quad [\text{Ag}^+] &= \sqrt{\frac{0.01}{9.072 \times 10^{14}}} \\
 &= \sqrt{1.099 \times 10^{-17}} \\
 &= \sqrt{10.099 \times 10^{-18}} \\
 &= \mathbf{3.178 \times 10^{-9} \text{ M}}
 \end{aligned}$$

SOLVED PROBLEM 12. Zinc granules are added in excess to 500 ml of 1.0 M nickel nitrate solution at 25 °C until the equilibrium is reached. If the standard reduction potential of Zn^{2+}/Zn and Ni^{2+}/Ni are -0.75 V and -0.24 V respectively, find out the concentrations of Ni^{2+} ions in the solution at equilibrium.

SOLUTION : (i) To calculate the emf of the cell

Formula used

$$\begin{aligned}
 E_{\text{cell}} &= E_{\text{right}} - E_{\text{Left}} \\
 &= (-0.24 \text{ V}) - (-0.75 \text{ V}) \\
 &= 0.51 \text{ V}
 \end{aligned}$$

(ii) To calculate the concentration of Ni^{2+} ions

Formula used

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Ni}^{2+}]}$$

Quantities given

$$E_{\text{cell}} (\text{at equilibrium}) = 0 \quad E_{\text{cell}}^{\circ} = 0.51 \text{ V} \quad n = 2$$

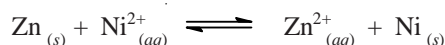
Substitution of values

$$0 = 0.51 - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Ni}^{2+}]}$$

$$\begin{aligned}
 \text{or} \quad \log \frac{[\text{Zn}^{2+}]}{[\text{Ni}^{2+}]} &= \frac{2 \times 0.51}{0.0591} \\
 &= 17.2589
 \end{aligned}$$

$$\begin{aligned}
 \text{or} \quad \frac{[\text{Zn}^{2+}]}{[\text{Ni}^{2+}]} &= \text{Antilog } 17.2589 \\
 &= 1.815 \times 10^{17}
 \end{aligned}$$

Let x be the concentration Ni^{2+} at equilibrium, we have



At Equilibrium $x \qquad 1-x$

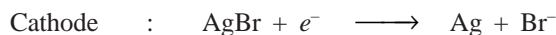
$$\text{or} \quad \frac{1-x}{x} = 1.815 \times 10^{17}$$

$$\text{or} \quad x = \mathbf{5.51 \times 10^{-18}}$$

SOLVED PROBLEM 13. For the galvanic cell

Calculate the emf generated and assign correct polarity to each electrode for a spontaneous process after taking into account the cell reaction at 25 °C. $K_{sp} \text{AgCl} = 2.8 \times 10^{-10}$, $K_{sp} \text{AgBr} = 3.3 \times 10^{-13}$.

SOLUTION : The cell reactions are



Formula used

$$\begin{aligned} E_{\text{cell}} &= E_{\text{right}} - E_{\text{left}} \\ &= \left[E^\circ - \frac{2.303}{nF} \log [\text{Ag}^+] \right] - \left[E^\circ - \frac{2.303}{nF} \log [\text{Ag}^+] \right] \end{aligned}$$

Quantities given

$$[\text{Ag}^+] \text{ in left hand electrode} = \frac{K_{sp} (\text{AgCl})}{[\text{Cl}^-]} = \frac{2.8 \times 10^{-10}}{0.2} = 1.4 \times 10^{-9} \text{ mol lit}^{-1}$$

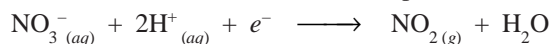
$$[\text{Ag}^+] \text{ in right hand electrode} = \frac{K_{sp} (\text{AgBr})}{[\text{Br}^-]} = \frac{3.3 \times 10^{-13}}{0.001} = 3.3 \times 10^{-10} \text{ mol lit}^{-1}$$

$$n = 1$$

Substitution of values

$$\begin{aligned} E_{\text{cell}} &= \left[E^\circ - \frac{2.303}{nF} \log 3.3 \times 10^{-10} \right] - \left[E^\circ - \frac{2.303}{nF} \log 1.4 \times 10^{-9} \right] \\ &= \frac{0.0591}{1} \log \frac{1.4 \times 10^{-9}}{3.3 \times 10^{-10}} \\ &= -0.037 \text{ V} \end{aligned}$$

Since E_{cell} is -ve, the cell reaction is non-spontaneous. The reverse reaction will be spontaneous.

SOLVED PROBLEM 14. The standard reduction potential for the half cell

is 0.78 V.

(i) Calculate the reduction potential in 8 M H^+ .

(ii) What will be the reduction potential of the half cell in neutral solution? Assume all other species to be at unit concentration.

SOLUTION : (i) To calculate the reduction potential in 8 M H^+ .

Formula used

$$E = E^\circ - \frac{0.059}{n} \log K$$

where

$$K = \frac{[\text{NO}_2] [\text{H}_2\text{O}]}{[\text{NO}_3^-] [\text{H}^+]}$$

Quantities gives

$$E^\circ = 0.78 \text{ V}$$

$$n = 1$$

$$[\text{H}^+] = 8 \text{ M}$$

Substitution of values

$$\begin{aligned} E &= 0.78 - \frac{0.0591}{1} \log \frac{1}{(8)^2} \\ &= 0.78 - 0.0591 \times (-1.806) \\ &= 0.78 + 0.1067 \\ &= \mathbf{0.8867 \text{ V}} \end{aligned}$$

(ii) To calculate the reduction potential of the half cell in neutral Solution

Formula used

$$E = E^\circ - \frac{0.0591}{1} \log \frac{1}{[H^+]}$$

Quantities given

$$E^\circ = 0.78 \text{ V}$$

$$n = 1$$

$$[H^+] = 10^{-7}$$

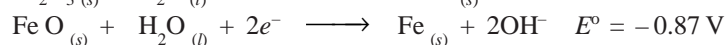
Substitution of values

$$\begin{aligned} E &= 0.78 - \frac{0.0591}{1} \log \frac{1}{(10^{-7})^2} \\ &= 0.78 - 0.0591 \times 14 \\ &= 0.78 - 0.8274 \\ &= \mathbf{-0.0474} \end{aligned}$$

SOLVED PROBLEM 15. The Edison storage cell is represented as



The half cell reactions are



(i) What is the cell emf ?

(ii) What is the maximum amount of electrical energy that can be obtained from one mole of Ni_2O_3 ?

SOLUTION : (i) To calculate the cell emf

Formula used

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}$$

Quantities given

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0.40 - (-0.87) = 1.27 \text{ V}$$

$$n = 1$$

$$[\text{Products}] = 1$$

$$[\text{Reactants}] = 1$$

Substitution of values

$$\begin{aligned} E_{\text{cell}} &= 1.27 \text{ V} - \frac{0.0591}{1} \log 1 \\ &= \mathbf{1.27 \text{ V}} \end{aligned}$$

(ii) To calculate the maximum amount of electrical energy that can be obtained from one mole of Ni_2O_3 ?

Formula used

$$W_{elect} = n F E$$

Quantities gives

$$n = 2$$

$$F = 96500$$

$$E = 1.27 \text{ V}$$

Substitution of values

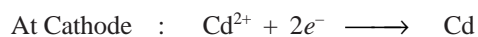
$$\begin{aligned} W_{elect} &= 2 \times 96500 \times 1.27 \\ &= \mathbf{2.451 \times 10^5 \text{ J}} \end{aligned}$$

SOLVED PROBLEM 16. Calculate EMF of the following cell at 20 °C ;



E° for Zinc and Cadmium electrodes are -0.76 and -0.40 volts respectively.

SOLUTION : The cell reactions are

**(i) To calculate E° of the cell****Formula used**

$$E_{cel}^\circ = E_{right}^\circ - E_{left}^\circ$$

Quantities given

$$E_{right}^\circ = -0.40$$

$$E_{left}^\circ = -0.76$$

Substitution of values

$$\begin{aligned} E_{cel}^\circ &= -0.40 - (-0.76 \text{ V}) \\ &= 0.36 \text{ V} \end{aligned}$$

(ii) To calculate EMF of the cell**Formula used**

$$E_{cell} = E_{cell}^\circ - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Cd}^{2+}]}$$

Quantities given

$$E_{cell}^\circ = 0.36 \text{ V}$$

$$n = 2$$

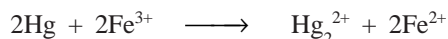
$$[\text{Zn}^{2+}] = 0.0004$$

$$[\text{Cd}^{2+}] = 0.2$$

Substitution of values

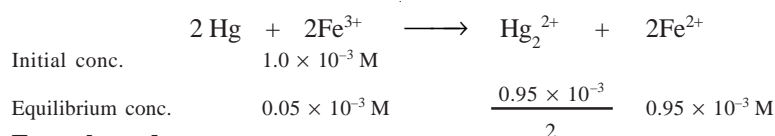
$$\begin{aligned} E_{cell} &= 0.36 - \frac{0.0591}{2} \log \frac{0.0004}{0.2} \\ &= 0.36 - 0.02955 \log 0.0002 \\ &= 0.36 - 0.02955 \times (-2.6989) \\ &= 0.36 + 0.07975 \\ &= \mathbf{0.4397 \text{ V}} \end{aligned}$$

SOLVED PROBLEM 17. An excess of liquid mercury is added to an acidified solution of $1.0 \times 10^{-3} \text{ M Fe}^{3+}$. It is found that 5% of Fe^{3+} remains at equilibrium at 25 °C. Calculate $E_{\text{Hg}^{2+}/\text{Hg}}^\circ$, assuming that the only reaction that occurs is



Given $E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^\circ = 0.77 \text{ V}$

SOLUTION : The cell reaction is



Formula used

$$E = \left[E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} - E_{\text{Hg}_2^{2+}/\text{Hg}}^{\circ} \right] - \frac{0.0591}{n} \log \frac{[\text{Hg}_2^{2+}] [\text{Fe}^{2+}]^2}{[\text{Fe}^{3+}]^2}$$

Quantities given

$$\begin{array}{lll}
 E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} = 0.77 \text{ V} & n = 2 & [\text{Hg}_2^{2+}] = \frac{0.95 \times 10^{-3}}{2} \\
 [\text{Fe}^{2+}] = 0.95 \times 10^{-3} & [\text{Fe}^{3+}] = 0.05 \times 10^{-3} & E = 0
 \end{array}$$

Substitution of values

$$\begin{aligned}
 E &= \left[0.77 - E_{\text{Hg}_2^{2+}/\text{Hg}}^{\circ} \right] - \frac{0.0591}{2} \log \frac{\frac{0.95 \times 10^{-3}}{2} \times (0.95 \times 10^{-3})^2}{(0.05 \times 10^{-3})^2} \\
 E_{\text{Hg}_2^{2+}/\text{Hg}}^{\circ} &= 0.77 - 0.02955 \log 0.00857 \\
 &= \mathbf{0.831 \text{ V}}
 \end{aligned}$$

ADDITIONAL PRACTICE PROBLEMS

- Calculate the maximum possible electric work that can be obtained from the following cell under standard conditions at 25 °C



Given $E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76 \text{ V}$ $E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} = 0.34 \text{ V}$

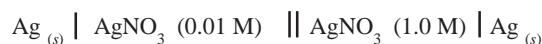
Answer. $-212.3 \text{ kJ mol}^{-1}$

- A Galvanic cell consists of metallic zinc plate immersed in 0.1 M zinc nitrate solution and lead plate in 0.02 M lead nitrate solution. Calculate the emf of the cell at 25 °C. Write the chemical equations of the electrode reactions.

$$E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76 \text{ V}, \quad E_{\text{Pb}^{2+}/\text{Pb}}^{\circ} = -0.13 \text{ V}$$

Answer. 0.6095 V

- For a cell



(a) Calculate the emf at 25 °C

(b) Will the cell generate emf when two concentrations become equal.

Answer. 0.1184 V, No

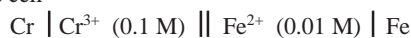
- Calculate the standard electrode potential of Ni^{2+}/Ni electrode, if the cell potential of the cell



is 0.59 V.

Answer. -0.2205 V

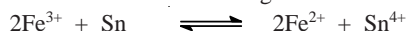
- Calculate the emf of the cell



Given $E_{\text{Cr}^{3+}/\text{Cr}}^{\circ} = 0.75 \text{ V}$ $E_{\text{Fe}^{2+}/\text{Fe}}^{\circ} = -0.45 \text{ V}$

Answer. 0.2607 V

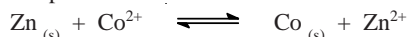
6. Determine the equilibrium constant of the following reaction at 298 K



From the obtained value of equilibrium constant predict whether Sn^{2+} ion can reduce Fe^{3+} to Fe^{2+} quantitatively or not.

Answer. 1.4215×10^{31}

7. The following reaction takes place in the cell



Write down the electrode reactions and calculate the standard emf of the cell. Given that

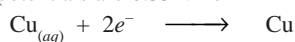
$$E^\circ_{\text{Zn}/\text{Zn}^{2+}} = 0.76 \text{ V}, E^\circ_{\text{Co}/\text{Co}^{2+}} = 0.28 \text{ V}$$

Answer. 0.48 V

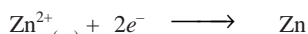
8. Consider the cell



The standard reduction potentials are 0.35 V for



and -0.763 V for



- (i) Write down the cell reactions
(ii) Calculate the emf of the cell
(iii) Is the cell reaction spontaneous or not ?

Answer. 1.113, spontaneous

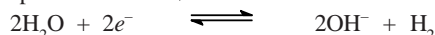
9. A cell contains two hydrogen electrodes. The negative electrode is in contact with solution of 10^{-6} M hydrogen ions. The emf of the cell is 0.118 volt at 25°C . Calculate the concentration of H^+ ion at positive electrode ?

Answer. $1 \times 10^{-4} \text{ M}$

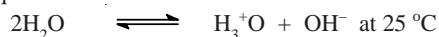
10. The standard reduction potential of Ag^+/Ag electrode at 298 K is 0.799 V. Given that for Ag I , $K_{sp} = 8.7 \times 10^{-17}$, evaluate the potential of the Ag^+/Ag electrode in a saturated solution of Ag I

Answer. 0.325 V

11. The standard reduction potential at 25°C of the reaction

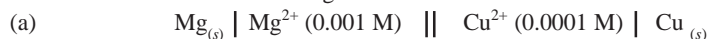


is -0.8277 V . Calculate the equilibrium constant for the reaction :



Answer. 1×10^{-14}

12. Calculate the emf of the following cells at 25°C



Given $E^\circ_{\text{Mg}^{2+}/\text{Mg}} = -2.37 \text{ V}$, $E^\circ_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$, $E^\circ_{\text{Fe}^{3+}/\text{Fe}} = -0.44 \text{ V}$

Answer. (a) 2.6805 V (b) -0.5286 V

13. Calculate the emf of a cell containing two hydrogen electrodes, the negative one is in contact with 10^{-6} M OH^- ions and the positive one is in contact with 0.05 M H^+ .

Answer. 0.395 V

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Photochemistry

CHAPTER

KEY CONCEPTS AND EQUATIONS



PHOTOCHEMICAL REACTION

A reaction which takes place by absorption of visible and ultraviolet radiations is called a photochemical reaction and the branch of chemistry which deals with the study of photochemical reactions is called Photochemistry.

LIGHT ABSORPTION

When light is passed through a medium, a part of it is absorbed. The photochemical reactions are caused by the absorbed light. The intensity of radiation can be defined as the number of photons that pass across a unit area in unit time. Mathematically,

$$\frac{dN}{N} = b dx = - \frac{dI}{I}$$

where N is the number of incident photons, dN , is the number of photons absorbed in thickness dx , I is the intensity of incident light, $-dI$ is the reduction in the intensity of incident light, and b is proportionately constant called absorption constant.

When $x = 0$, $I = I_0$. On integration we get

$$I = I_0(-bx)$$

or

$$\ln \left(\frac{I}{I_0} \right) = -bx$$

This relationship is called **Lambert Law**.

This equation was extended to solution of compounds in transparent solvent and takes the form

$$\ln \left(\frac{I}{I_0} \right) = \epsilon Cx$$

where c is the molar concentration, ϵ is a constant characteristic of the solute called the absorption coefficient. This new relationship is called **Lambert-Beer Law**.

LAWS OF PHOTOCHEMISTRY

Grothus-Draper Law

According to this law it is only the absorbed light radiations that are effective in producing a

chemical reaction. This law is purely qualitative in nature. It gives no idea of the relation between the absorbed radiation and molecules undergoing change.

Stark Einstein Law

According to this law each molecule of the reacting substance absorbs a single photon of radiation causing the reaction and is activated to form the product in a photochemical reaction.

QUANTUM YIELD OR QUANTUM EFFICIENCY

The number of molecules reacted or formed per photon of light absorbed is called Quantum yield. It is denoted by ϕ so that

$$\phi = \frac{\text{No. of molecules reacted or formed}}{\text{No. of photons absorbed.}}$$

THE ENERGY OF PHOTONS : EINSTEIN

The energy of a photon (or quantum), E , is given by the equation

$$E = h\nu = \frac{h\nu}{\lambda}$$

where h is Planck's constant (6.625×10^{-27}), ν is the frequency of radiation, λ is the wavelength of radiation and c is the velocity of light (3.0×10^{10} cm sec $^{-1}$) The energy, E , of an Avogadro's Number (N) of photons is referred to as one einstein. That is

$$E = \frac{N h c}{\lambda}$$

Substituting $N = 6.02 \times 10^{23}$, $h = 6.625 \times 10^{-27}$ and $c = 3.0 \times 10^{10}$ cm sec $^{-1}$, we have

$$E = \frac{1.196 \times 10^8}{\lambda} \text{ erg mol}^{-1}$$

If λ is expressed in Å unit ($1 \text{ Å} = 10^{-8}$ cm), we get

$$E = \frac{1.196 \times 10^{16}}{\lambda} \text{ erg mol}^{-1}$$

since $1 \text{ cal} = 4.184 \times 10^7$ erg, energy in calories would be

$$\begin{aligned} E &= \frac{1.196 \times 10^{16}}{\lambda \times 4.184 \times 10^7} \text{ cal mol}^{-1} \\ &= \frac{2.859 \times 10^5}{\lambda} \text{ cal mol}^{-1} \end{aligned}$$

It is clear that numerical value of einstein varies inversely with the wavelength¹⁰ of radiations.

ADDITIONAL PRACTICE PROBLEMS

SOLVED PROBLEM 1. Calculate the energy of one einstein of a light of wavelength 3000 Å.

SOLUTION :

Formula used

$$E = \frac{2.859 \times 10^5}{\lambda} \text{ kcal mol}^{-1}$$

Quantity given

$$\lambda = 3000 \text{ Å}$$

Substitution of value

$$\begin{aligned} E &= \frac{2.859 \times 10^5}{3000} \\ E &= 95.3 \text{ kcal mol}^{-1} \end{aligned}$$

SOLVED PROBLEM 2. Calculate the energy of a photon corresponding to wavelength 3600 Å.

($h = 6.63 \times 10^{-27}$ erg sec ; $c = 3 \times 10^{10}$ cm sec⁻¹)

SOLUTION :

Formula used

$$E = \frac{hc}{\lambda}$$

Quantities given

$$h = 6.63 \times 10^{-27} \text{ erg sec} \quad c = 3 \times 10^{10} \text{ cm sec}^{-1} \quad \lambda = 3600 \text{ Å} = 3600 \times 10^{-8} \text{ cm}$$

Substitution of values

$$\begin{aligned} E &= \frac{6.63 \times 10^{-27} \times 3 \times 10^{10}}{3600 \times 10^{-8}} \text{ erg} \\ &= \frac{19.89 \times 10^{-17}}{10^{-8} \times 3600 \times 4.184 \times 10^7} \text{ cal} \quad [\because 1 \text{ cal} = 4.184 \times 10^7 \text{ erg}] \\ &= \mathbf{1.320 \times 10^{-19} \text{ cal}} \end{aligned}$$

SOLVED PROBLEM 3. A radiation of 2530 Å incident on HI results in the decomposition of 1.85×10^{-2} mole per 1000 cal of radiant energy. Calculate the quantum efficiency.

($N = 6.023 \times 10^{23}$; $h = 6.62 \times 10^{-27}$; $c = 3 \times 10^{10}$ cm sec⁻¹)

SOLUTION : (i) To calculate the number of einsteins absorbed

Formula used

$$\text{No. of einsteins absorbed} = \frac{\text{Total Energy absorbed}}{\frac{N h c}{\lambda}}$$

Quantities given

$$\begin{aligned} \text{Total energy absorbed} &= 1000 \text{ cal} = 1000 \times 4.184 \times 10^7 \text{ erg} & N &= 6.023 \times 10^{23} \\ h &= 6.62 \times 10^{-27} & c &= 3 \times 10^{10} & \lambda &= 2530 \text{ Å} = 2530 \times 10^{-8} \text{ cm} \end{aligned}$$

Substitution of values

$$\begin{aligned} \text{No. of einstein absorbed} &= \frac{1000 \times 4.184 \times 10^7 \times 2530 \times 10^{-8}}{6.023 \times 10^{23} \times 6.62 \times 10^{-27} \times 3 \times 10^{10}} \\ &= 8.849 \times 10^{-3} \end{aligned}$$

(ii) To calculate the quantum efficiency

Formula used

$$\phi = \frac{\text{No. of moles of HI decomposed}}{\text{No. of einsteins absorbed}}$$

Quantities given

$$\begin{aligned} \text{No. of moles of HI decomposed} &= 1.85 \times 10^{-2} \text{ mole} \\ \text{No. of einsteins absorbed} &= 8.849 \times 10^{-3} \end{aligned}$$

Substitution of values

$$\begin{aligned} \phi &= \frac{1.85 \times 10^{-2}}{8.849 \times 10^{-3}} \\ &= \mathbf{2.09} \end{aligned}$$

SOLVED PROBLEM 4. Calculate the value of one einstein for light having $\lambda = 2000$ Å.

SOLUTION :

Formula used

$$E = \frac{2.859 \times 10^5}{\lambda}$$

Quantity given

$$\lambda = 2000 \text{ \AA}$$

Substitution of values

$$E = \frac{2.859 \times 10^5}{2000}$$

$$= 142.95 \text{ kcal}$$

SOLVED PROBLEM 5. If the value of an einstein is 1.594×10^4 kJ, find the value of wavelength of radiation.

SOLUTION :**Formula used**

$$\text{Energy per einstein} = \frac{N h c}{\lambda}$$

Quantities given

$$\begin{aligned} \text{Energy per einstein} &= 1.594 \times 10^4 \text{ kJ} & c &= 3 \times 10^{10} \text{ cm sec}^{-1} \\ &= 1.594 \times 10^{14} \text{ erg} \\ h &= 6.62 \times 10^{-27} \text{ erg sec} & N &= 6.02 \times 10^{23} \end{aligned}$$

Substitution of values

$$\begin{aligned} 1.594 \times 10^{14} \text{ kJ} &= \frac{6.02 \times 10^{23} \times 6.62 \times 10^{-27} \text{ erg sec} \times 3 \times 10^{10} \text{ cm sec}^{-1}}{\lambda} \\ \lambda &= \frac{119.55 \times 10^6}{1.594 \times 10^{14}} \\ &= 75 \times 10^{-8} \text{ cm} \\ &= 75 \text{ \AA} \end{aligned}$$

SOLVED PROBLEM 6. Calculate the energy of the photon corresponding to wavelength 4800 Å. ($h = 6.624 \times 10^{-27}$ erg sec ; $c = 3 \times 10^{10}$ cm sec⁻¹)

SOLUTION :**Formula used**

$$E = \frac{h c}{\lambda}$$

Quantities given

$$h = 6.624 \times 10^{-27} \text{ erg sec} \quad c = 3 \times 10^{10} \text{ cm sec}^{-1} \quad \lambda = 4800 \text{ \AA} = 4800 \times 10^{-8} \text{ cm}$$

Substitution of values

$$\begin{aligned} E &= \frac{6.624 \times 10^{-27} \times 3 \times 10^{10}}{4800 \times 10^{-8}} \text{ erg} \\ &= 4.14 \times 10^{-12} \text{ erg} \\ &= \frac{4.14 \times 10^{-12}}{4.184 \times 10^7} \text{ cal} \quad [1 \text{ cal} = 4.184 \times 10^7 \text{ erg}] \\ &= 0.9895 \times 10^{-19} \text{ cal} \\ &= 0.9895 \times 10^{-22} \text{ kcal} \end{aligned}$$

SOLVED PROBLEM 7. In the photochemical reaction $B \longrightarrow C$, 1.00×10^{-5} mole of C is formed as a result of the absorption of 6.00×10^7 ergs at 3600 Å. Calculate the quantum yield.

SOLUTION :**Formula used**

$$\text{Quantum efficiency} = \frac{\text{No. of moles of C formed}}{\text{No. of einsteins absorbed}}$$

Quantities given

$$\text{No. of moles of C formed} = 1.00 \times 10^{-5} \text{ mole}$$

$$\begin{aligned} \text{No. of einsteins absorbed} &= \frac{\text{Energy absorbed}}{\text{Energy per einstein}} \\ &= \frac{6.0 \times 10^7 \text{ erg}}{\frac{1.196 \times 10^{16} \text{ erg}}{\lambda}} \\ &= \frac{6.0 \times 10^7 \times 3600}{1.196 \times 10^{16}} \quad [\because \lambda = 3600 \text{ \AA}] \\ &= 1.806 \times 10^{-5} \end{aligned}$$

Substitution of values

$$\begin{aligned} \text{Quantum efficiency, } \phi &= \frac{1.00 \times 10^{-5}}{1.806 \times 10^{-5}} \\ &= \mathbf{0.553} \end{aligned}$$

SOLVED PROBLEM 8. For a photochemical reaction $A \longrightarrow B$, 1.0×10^{-5} mole of B were formed on absorption of 6.0×10^7 ergs at 3600 \AA . Calculate the quantum efficiency of the reaction. ($N = 6.62 \times 10^{23}$; $h = 6.62 \times 10^{-27} \text{ erg sec}$)

SOLUTION :**Formula used**

$$\text{Quantum efficiency} = \frac{\text{No. of moles of B formed}}{\text{No. of einsteins absorbed}}$$

Quantities given

$$\text{No. of moles of B formed} = 1.00 \times 10^{-5} \text{ mole}$$

$$\begin{aligned} \text{No. of einsteins absorbed} &= \frac{\text{Energy absorbed}}{\text{Energy per einstein}} \\ &= \frac{6.0 \times 10^7 \text{ erg}}{\frac{1.196 \times 10^{16} \text{ erg}}{\lambda}} \quad [\because 1 \text{ einstein} = \frac{1.196 \times 10^{16} \text{ erg}}{\lambda}] \\ &= \frac{6.0 \times 10^7 \times 3600}{1.196 \times 10^{16}} \quad [\because \lambda = 3600 \text{ \AA}] \\ &= 1.806 \times 10^{-5} \end{aligned}$$

Substitution of values

$$\begin{aligned} \text{Quantum efficiency, } \phi &= \frac{1.0 \times 10^{-5}}{1.806 \times 10^{-5}} \\ &= \mathbf{0.553} \end{aligned}$$

SOLVED PROBLEM 9. A certain system absorbs 2×10^{16} quanta of light per second. On irradiation for 10 minutes 0.001 mole of the reactant was found to have reacted. Calculate quantum yield for the process. (Avogadro's No. = 6.024×10^{23})

SOLUTION :**Formula used**

$$\phi = \frac{\text{No. of molecules decomposed}}{\text{No. of photons absorbed}}$$

Quantities given

$$\begin{aligned}\text{No. of molecules decomposed} &= 0.001 \times 6.024 \times 10^{23} \text{ molecules} \\ \text{No. of photons absorbed in 10 minutes} &= \text{No. of photons absorbed per second} \times \text{No. of seconds} \\ &= 2 \times 10^{16} \times 600\end{aligned}$$

Substitution of values

$$\begin{aligned}\phi &= \frac{0.001 \times 6.024 \times 10^{23}}{2 \times 10^{16} \times 600} \\ &= \mathbf{50.2}\end{aligned}$$

SOLVED PROBLEM 10. Calculate the values of frequency, quantum energy and einstein for 500 nm radiation.

SOLUTION : (i) To calculate the value of frequency**Formula used**

$$\nu = \frac{c}{\lambda}$$

Quantities given

$$c = 3 \times 10^{10} \text{ cm sec}^{-1} \quad \lambda = 500 \text{ nm} = 500 \times 10^{-9} \text{ m} = 500 \times 10^{-7} \text{ cm}$$

Substitution of values

$$\begin{aligned}\nu &= \frac{3 \times 10^{10}}{500 \times 10^{-7}} \\ &= \mathbf{6 \times 10^{14}}\end{aligned}$$

(ii) To calculate the quantum energy**Formula used**

$$E = \frac{h c}{\lambda}$$

Quantities given

$$h = 6.62 \times 10^{-27} \text{ erg sec} \quad c = 3 \times 10^{10} \text{ cm sec}^{-1} \quad \lambda = 500 \times 10^{-7} \text{ cm}$$

Substitution of values

$$\begin{aligned}E &= \frac{6.62 \times 10^{-27} \times 3 \times 10^{10}}{500 \times 10^{-7}} \\ &= \mathbf{39.72 \times 10^{-13} \text{ erg}}\end{aligned}$$

(iii) To calculate the value of one einstein**Formula used**

$$\text{Energy per einstein} = \text{Avogadro's No.} \times \text{Energy per photon}$$

Quantities given

$$\text{Avogadro's No.} = 6.02 \times 10^{23} \quad \text{Energy per photon} = 39.72 \times 10^{-11} \text{ erg}$$

Substitution of values

$$\begin{aligned}\text{Energy per einstein} &= 6.02 \times 10^{23} \times 39.72 \times 10^{-11} \text{ erg} \\ &= 2.39 \times 10^{14} \text{ erg mol}^{-1} \\ &= \frac{2.39 \times 10^{14}}{4.184 \times 10^7} \text{ cal mol}^{-1} \quad [\because 1 \text{ cal} = 4.184 \times 10^7 \text{ erg}] \\ &= 5.71 \times 10^6 \text{ cal mol}^{-1} \\ &= \mathbf{5.71 \times 10^3 \text{ kcal mol}^{-1}}\end{aligned}$$

SOLVED PROBLEM 11. In a photochemical combination of H_2 and Cl_2 a quantum yield of 1×10^6 is obtained with a wavelength of 4800 \AA . How many moles of HCl would be produced under these conditions per calorie of radiation energy absorbed ?

SOLUTION : (i) To calculate no. of einsteins absorbed per cal of energy

Formula used

$$\text{No. of einsteins} = \frac{\text{Energy absorbed}}{\text{Energy per einstein}}$$

Quantities given

$$\text{Energy absorbed} = 1 \text{ cal} = 4.184 \times 10^7 \text{ erg}$$

$$\text{Energy per einstein} = \frac{1.196 \times 10^{16}}{\lambda} \text{ erg mol}^{-1}$$

$$\lambda = 4800 \text{ \AA}$$

Substitution of values

$$\begin{aligned} \text{No. of einsteins} &= \frac{4.184 \times 10^7 \text{ erg} \times 4800}{1.196 \times 10^{16} \text{ erg mol}^{-1}} \\ &= 1.679 \times 10^{-5} \end{aligned}$$

(ii) To calculate the no. of moles of HCl produced

Formula used

$$\phi = \frac{\text{No. of moles of HCl produced}}{\text{No. of einsteins absorbed}}$$

Quantities given

$$\phi = 1 \times 10^6 \quad \text{No. of einsteins absorbed} = 1.679 \times 10^{-5}$$

Substitution of values

$$1 \times 10^6 = \frac{\text{No. of moles of HCl produced}}{1.679 \times 10^{-5}}$$

$$\text{or No. of moles of HCl produced} = \mathbf{16.79 \text{ moles}}$$

SOLVED PROBLEM 12. Calculate the energy in electron volt (eV) units of quantum of radiation of wavelength 1000 \AA .

$$\text{Velocity of light} = 3.0 \times 10^{10} \text{ cm sec}^{-1}$$

$$h = 6.62 \times 10^{-27} \text{ erg sec}$$

$$1 \text{ \AA} = 10^{-8} \text{ cm}$$

$$1 \text{ eV} = 1.6 \times 10^{-12} \text{ erg}$$

SOLUTION :

Solution :

Formula used

$$E = \frac{h c}{\lambda}$$

Quantities given

$$h = 6.62 \times 10^{-27} \text{ erg sec} \quad c = 3.0 \times 10^{10} \text{ cm sec}^{-1} \quad \lambda = 1000 \text{ \AA} = 1000 \times 10^{-8} \text{ cm}$$

Substitution of values

$$\begin{aligned} E &= \frac{6.62 \times 10^{-27} \times 3 \times 10^{10}}{1000 \times 10^{-8}} \text{ erg} \\ &= 1.986 \times 10^{-11} \text{ erg} \\ &= \frac{1.986 \times 10^{-11}}{1.6 \times 10^{-12}} \text{ eV} \quad [1 \text{ eV} = 1.6 \times 10^{-12} \text{ erg}] \\ &= \mathbf{12.4125 \text{ eV}} \end{aligned}$$

SOLVED PROBLEM 13. A certain system absorbs 3×10^8 quanta of light per second. On irradiation for 400 seconds, 0.001 mole of the reactant was found to have reacted. Calculate the quantum yield for the process (Avogadro's No. = 6.02×10^{23}).

SOLUTION :

Formula used

$$\phi = \frac{\text{No. of molecules reacted}}{\text{No. of photons of radiation energy absorbed}}$$

Quantities given

$$\begin{aligned} \text{No. of molecules reacted} &= 0.001 \times 6.02 \times 10^{23} \\ \text{No. of photons of energy absorbed} &= \text{No. of photons absorbed per second} \times \text{No. of seconds} \\ &= 3 \times 10^8 \times 400 \end{aligned}$$

Substitution of values

$$\begin{aligned} \phi &= \frac{0.001 \times 6.02 \times 10^{23}}{3 \times 10^8 \times 400} \\ &= 50.16 \times 10^8 \end{aligned}$$

SOLVED PROBLEM 14. The quantum yield for reaction $2 \text{HI} \longrightarrow \text{H}_2 + \text{I}_2$ is 2. Calculate the number of photons absorbed in an experiment in which 0.01 mole of HI are decomposed. ($N = 6.02 \times 10^{23}$)

SOLUTION :

Formula used

$$\phi = \frac{\text{No. of molecules reacted}}{\text{No. of photons absorbed}}$$

Quantities given

$$\phi = 2 \quad \text{No. of molecules reacted} = 0.01 \times 6.02 \times 10^{23}$$

Substitution of values

$$\begin{aligned} 2 &= \frac{0.01 \times 6.02 \times 10^{23}}{\text{No. of photons absorbed}} \\ \text{No. of photons absorbed} &= \frac{0.01 \times 6.02 \times 10^{23}}{2} \\ &= 3.01 \times 10^{21} \end{aligned}$$

SOLVED PROBLEM 15. Derive value of radiation of wavelength 3000 \AA in :

(i) Wave number (ii) Frequency (iii) Quantum energy (iv) Einstein energy

SOLUTION : (i) To calculate wave number

Formula used

$$\bar{\nu} = \frac{1}{\lambda}$$

Quantity given

$$\lambda = 3000 \text{ \AA} = 3000 \times 10^{-8} \text{ cm}$$

Substitution of value

$$\begin{aligned} \bar{\nu} &= \frac{1}{3000 \times 10^{-8} \text{ cm}} \\ &= 3.33 \times 10^4 \text{ cm}^{-1} \end{aligned}$$

(ii) To calculate frequency

Formula used

$$\nu = \frac{c}{\lambda}$$

Quantities given

$$c = 3 \times 10^{10} \text{ cm sec}^{-1}$$

$$\lambda = 3000 \text{ \AA} = 3000 \times 10^{-8} \text{ cm}$$

Substitution of values

$$\begin{aligned} \nu &= \frac{3 \times 10^{10} \text{ cm sec}^{-1}}{3000 \times 10^{-8} \text{ cm}} \\ &= 1 \times 10^{15} \text{ sec}^{-1} \end{aligned}$$

(iii) To calculate quantum energy.**Formula used**

$$E = \frac{hc}{\lambda}$$

Quantities given

$$h = 6.62 \times 10^{-27} \text{ erg sec} \quad c = 3 \times 10^{10} \text{ cm sec}^{-1} \quad \lambda = 3000 \times 10^{-8} \text{ cm}$$

Substitution of values

$$\begin{aligned} E &= \frac{6.62 \times 10^{-27} \times 3 \times 10^{10}}{3000 \times 10^{-8}} \text{ erg} \\ &= 5.516 \times 10^{-12} \text{ erg} \end{aligned}$$

(iv) To calculate Einstein energy**Formula used**

$$\text{Einstein energy} = \text{Avogadro's No.} \times \text{Quantum energy}$$

Quantities given

$$\text{Avogadro's No.} = 6.02 \times 10^{23} \quad \text{Quantum energy} = 6.62 \times 10^{-12} \text{ erg}$$

Substitution of values

$$\begin{aligned} E &= 6.02 \times 10^{23} \times 6.62 \times 10^{-12} \text{ erg} \\ &= 3.985 \times 10^{12} \text{ erg} \\ &= \frac{3.985 \times 10^{12}}{4.184 \times 10^7} \text{ cal} \quad [\because 1 \text{ cal} = 4.184 \times 10^7 \text{ erg}] \\ &= 9.524 \times 10^4 \text{ kcal} \end{aligned}$$

SOLVED PROBLEM 16. A substance in a cell of length l absorbs 20% of the incident light.

What fraction of light will be absorbed in a cell of length $5l$.

SOLUTION :**Formula used**

$$\log \frac{I}{I_o} = \frac{-kx}{2.303}$$

Quantities given

$$\frac{I}{I_o} = 100 - 20\% = 80\% = 0.8 \quad x = l \text{ in first case} \quad x = 5l \text{ in second case}$$

Substitution of values

$$\log A = \frac{-k \times l}{2.303} \quad \dots\text{(i) for first case}$$

$$\log A = \frac{-k \times 5l}{2.303} \quad \dots\text{(ii) for second case}$$

Dividing (i) by (ii) we get

$$\frac{\log 0.8}{\log A} = \frac{-k \times l}{2.303} \times \frac{2.303}{-k \times 5l}$$

or

$$\log A = 5 \times \log 0.8$$

$$= 5 \times (-0.0969)$$

$$= -0.4845$$

or

$$A = \text{Antilog}(-0.4845) = 0.3277 = 32.77\%$$

SOLVED PROBLEM 17. A certain system absorbs 8.81×10^8 ergs of radiation of the wavelength 2540 \AA in a certain time. It is observed that 1.12×10^{-4} moles of the irradiated substance has reacted in the same time. What is the quantum efficiency of the process ?

$$N = 6.023 \times 10^{23} \quad h = 6.625 \times 10^{-27} \quad c = 2.998 \times 10^{10} \text{ cm sec}^{-1}$$

SOLUTION : (i) To calculate the energy per einstein

Formula used

$$\text{Energy per einstein} = \frac{N h c}{\lambda}$$

Quantity given

$$N = 6.02 \times 10^{23} \quad h = 6.62 \times 10^{-27} \text{ erg sec} \quad c = 2.998 \times 10^{10} \text{ cm sec}^{-1} \quad \lambda = 2540 \times 10^{-8} \text{ cm}$$

Substitution of values

$$\begin{aligned} \text{Energy per einstein} &= \frac{6.02 \times 10^{23} \times 6.62 \times 10^{-27} \times 2.998 \times 10^{10}}{2540 \times 10^{-8}} \\ &= 4.70 \times 10^{12} \text{ erg} \end{aligned}$$

(ii) To calculate the quantum efficiency

Formula used

$$\phi = \frac{\text{No. of molecules reacted}}{\text{No. of einsteins absorbed}}$$

Quantities given

$$\text{No. of molecules reacted} = 1.12 \times 10^{-4} \text{ mole}$$

$$\begin{aligned} \text{No. of einsteins absorbed} &= \frac{\text{Energy absorbed}}{\text{Energy per einstein}} \\ &= \frac{8.81 \times 10^8 \text{ erg}}{4.70 \times 10^{12} \text{ erg}} \\ &= 1.874 \times 10^{-4} \end{aligned}$$

Substitution of values

$$\begin{aligned} \phi &= \frac{1.12 \times 10^{-4}}{1.874 \times 10^{-4}} \\ &= \mathbf{0.5977} \end{aligned}$$

SOLVED PROBLEM 18. Radiation of wavelength of 2500 \AA was passed through a cell containing 10 ml of a solution which was 0.05 molar in oxalic acid and 0.01 molar in uranyl sulphate. After absorption of 80 joules of radiation energy the concentration of oxalic acid was reduced to 0.04 molar. Calculate the quantum yield for the photochemical decomposition of oxalic acid at the given wavelength.

SOLUTION : (i) To calculate the number of photons absorbed

Formula used

$$\text{No. of photons absorbed} = \frac{\text{Energy absorbed}}{\text{Energy per photon}}$$

Quantities given

$$\text{Energy absorbed} = 80 \text{ Joules}$$

$$\begin{aligned} \text{Energy per photon} &= \frac{h c}{\lambda} = \frac{6.62 \times 10^{-27} \times 3 \times 10^{10}}{2500 \times 10^{-8} \times 10^7} \text{ J} \\ &= 7.944 \times 10^{-19} \text{ J} \end{aligned}$$

Substitution of values

$$\begin{aligned}\text{No. of photon absorbed} &= \frac{80\text{J}}{7.944 \times 10^{-19}\text{J}} \\ &= 1.007 \times 10^{20}\end{aligned}$$

(ii) To calculate the quantum efficiency**Formula used**

$$\text{Quantum efficiency} = \frac{\text{No. of molecules decomposed}}{\text{No. of photons absorbed}}$$

Quantities given

$$\begin{aligned}\text{No. of photons absorbed} &= 1.007 \times 10^{20} \\ \text{No. of molecules decomposed} &= \frac{0.01 \times 10 \times 6.02 \times 10^{23}}{1000} \\ &= 6.02 \times 10^{19}\end{aligned}$$

Substitution of values

$$\begin{aligned}\text{Quantum efficiency} &= \frac{6.02 \times 10^{19}}{1.007 \times 10^{20}} \\ &= \mathbf{0.598}\end{aligned}$$

SOLVED PROBLEM 19. A certain system absorbs 3.0×10^{16} quantum of light per second on irradiation for 10 minutes. 0.002 mole of reactant was found to have reacted. Calculate the quantum efficiency of the process. ($N = 6.023 \times 10^{23}$)

SOLUTION :**Formula used**

$$\phi = \frac{\text{No. of molecules reacted}}{\text{No. of einsteins absorbed}}$$

Quantities given

$$\begin{aligned}\text{No. of molecules reacted} &= 0.002 \times 6.023 \times 10^{23} \\ \text{No. of photons absorbed} &= 3.0 \times 10^{16} \times 600\end{aligned}$$

Substitution of values

$$\begin{aligned}\phi &= \frac{0.002 \times 6.023 \times 10^{23}}{3.0 \times 10^{16} \times 600} \\ &= \mathbf{66.92}\end{aligned}$$

SOLVED PROBLEM 20. 10% incident light is transmitted after passing through 2 cm thick glass. If glass is 1 cm thick, then how much light is absorbed of the same wavelength ?

SOLUTION :**Formula used**

$$\log \frac{I}{I_o} = \frac{-kcx}{2.303}$$

Quantities given

$$\frac{I}{I_o} = 10\% = \frac{10}{100} = 0.1 \quad x = 2 \text{ cm (in first case)} \quad x = 1 \text{ cm (in second case)}$$

Substitution of values

$$\log 0.1 = - \frac{k \times c \times 2}{2.303} \quad \dots\text{(i) for first case}$$

$$\text{and} \quad \log A = - \frac{k \times c \times 1}{2.303} \quad \dots\text{(ii) for second case}$$

Dividing (i) by (ii) we get

$$\frac{\log 0.1}{\log A} = \frac{-k \times c \times 2}{2.303} \times \frac{2.303}{-k \times c \times 1}$$

$$\frac{\log 0.1}{\log A} = 2$$

$$\text{or } \log A = \frac{\log 0.1}{2}$$

$$= -0.5$$

$$A = \text{Antilog}(-0.5) = 0.3162$$

$$= 31.62 \%$$

$$\text{Thus the amount absorbed} = 100 - 31.62$$

$$= \mathbf{68.38 \%}$$

SOLVED PROBLEM 21. When irradiated with light of wavelength 5000 Å, 1×10^{-4} mole of a substance decomposed. How many photons are absorbed during the reaction if its quantum efficiency is 10.0 (Avogadro's number = 6.02×10^{23})

SOLUTION :

Formula used

$$\text{Quantum yield, } \phi = \frac{\text{No. of molecules reacted}}{\text{No. of photons absorbed}}$$

Quantities given

$$\phi = 10.0$$

$$\text{No. of molecules reacted} = 1 \times 10^{-4} \times 6.02 \times 10^{23}$$

Substitution of values

$$10.0 = \frac{1.0 \times 10^{-4} \times 6.02 \times 10^{23}}{\text{No. of photons absorbed}}$$

$$\text{or No. of photons absorbed} = \frac{1.0 \times 10^{-4} \times 6.02 \times 10^{23}}{10}$$

$$= \mathbf{6.02 \times 10^{18}}$$

SOLVED PROBLEM 22. If one mole of a compound absorbs light of wavelength 2537 Å, calculate the amount of energy absorbed in kilo joules per mole.

SOLUTION :

Formula used

$$\text{Energy absorbed} = \frac{N h c}{\lambda}$$

Quantities given

$$N = 6.02 \times 10^{23}$$

$$h = 6.62 \times 10^{-27} \text{ erg sec}$$

$$c = 3.0 \times 10^{10} \text{ cm sec}^{-1}$$

$$\lambda = 2537 \text{ Å} = 2537 \times 10^{-8} \text{ cm}$$

Substitution of values

$$= \frac{6.02 \times 10^{23} \times 6.62 \times 10^{-27} \times 3 \times 10^{10}}{2537 \times 10^{-8}}$$

$$= 4.7125 \times 10^{12} \text{ erg}$$

$$= 4.7125 \times 10^5 \text{ J}$$

$$= 4.7125 \times 10^2 \text{ kJ}$$

$$= \mathbf{471.25 \text{ kJ}}$$

SOLVED PROBLEM 23. On passing through 1 cm long in a solution of concentration of 10^{-3} M, the incident ray is 10% absorbed. What will be the concentration of the solution which absorbs 90% of incident of radiation in the same cell.

SOLUTION :**Formula used**

$$\log \frac{I}{I_o} = \frac{-kcx}{2.303}$$

Quantities given

$$I/I_o = 100 - 10 = 90\% = 0.9$$

$$c = 1 \times 10^{-3} \text{ M in first case}$$

$$I/I_o = 100 - 90 = 10\% = 0.1$$

$$c = ? \text{ in second case}$$

Substitution of values

$$\log 0.9 = \frac{-k \times 1 \times 10^{-3} \times x}{2.303} \quad \dots(i) \text{ for first case}$$

$$\log 0.1 = \frac{-k \times c \times x}{2.303} \quad \dots(ii) \text{ for second case}$$

Dividing (i) by (ii) we get

$$\frac{\log 0.9}{\log 0.1} = \frac{-k \times 1 \times 10^{-3} \times x}{-k \times c \times x} \times \frac{2.303}{2.303}$$

$$\frac{-0.04575}{-1} = \frac{1 \times 10^{-3}}{c}$$

or

$$c = \frac{1 \times 10^{-3}}{0.04575} = 2.18 \times 10^{-2} \text{ M}$$

SOLVED PROBLEM 24. In the photochemical reaction between chlorine and hydrogen, 3×10^{-10} mole of chlorine have been converted into hydrochloric acid by irradiation with light of wavelength 3500 \AA . What is the quantum yield of the reaction if the light energy absorbed by the system is $7.16 \times 10^{-15} \text{ kcal}$?

SOLUTION : (i) To calculate the number of photons absorbed**Formula used**

$$\text{No. of photons absorbed} = \frac{\text{Energy absorbed}}{\frac{hc}{\lambda}}$$

Quantities given

$$\text{Energy absorbed} = 7.16 \times 10^{-15} \text{ kcal} = 7.16 \times 10^{-15} \times 10^3 \text{ cal}$$

$$= 7.16 \times 10^{-15} \times 10^3 \times 4.184 \times 10^7 \text{ erg}$$

$$h = 6.62 \times 10^{-27} \text{ erg sec} \quad c = 3 \times 10^{10} \text{ cm sec}^{-1} \quad \lambda = 3500 \text{ \AA} = 3500 \times 10^{-8} \text{ cm}$$

Substitution of values

$$\begin{aligned} \text{No. of photons absorbed} &= \frac{7.16 \times 10^{-15} \times 10^3 \times 4.184 \times 10^7}{\frac{6.62 \times 10^{-27} \times 3 \times 10^{10}}{3500 \times 10^{-8}}} \\ &= 5.28 \times 10^7 \end{aligned}$$

(ii) To calculate the quantum efficiency

$$\phi = \frac{\text{No. of molecules } \text{Cl}_2 \text{ reacted}}{\text{No. of photons absorbed}}$$

Quantities given

$$\text{No. of molecules of } \text{Cl}_2 \text{ reacted} = 3 \times 10^{-10} \text{ mole}$$

$$= 3 \times 10^{-10} \times 6.02 \times 10^{23}$$

$$\text{No. of photons absorbed} = 5.28 \times 10^7$$

Substitution of values

$$\phi = \frac{3 \times 10^{-10} \times 6.02 \times 10^{23}}{5.28 \times 10^7}$$

$$= 3.42 \times 10^6$$

SOLVED PROBLEM 25. Calculate the value of an einstein in kJ mol⁻¹ for radiation of wavelength 4500 Å.

SOLUTION :**Formula used**

$$E = \frac{N h c}{\lambda}$$

Quantities given

$$N = 6.02 \times 10^{23}$$

$$h = 6.62 \times 10^{-27} \text{ erg sec}$$

$$c = 3 \times 10^{10} \text{ cm sec}^{-1}$$

$$\lambda = 4500 \text{ Å} = 4500 \times 10^{-8} \text{ cm}$$

Substitution of values

$$E = \frac{6.02 \times 10^{23} \times 6.62 \times 10^{-27} \times 3 \times 10^{10}}{4500 \times 10^{-8}}$$

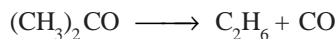
$$= 2.656 \times 10^{12} \text{ erg}$$

$$= \frac{2.656 \times 10^{12}}{10^7} \text{ J}$$

$$= \frac{2.656 \times 10^{12}}{10^7 \times 10^3} \text{ kJ}$$

$$= 265.68 \text{ kJ}$$

SOLVED PROBLEM 26. Acetone can be photolysed by irradiating with light of $\lambda = 3100 \text{ Å}$ according to the reaction



In an experiment the vessel containing acetone absorbs 0.001 J per second and yields 3×10^{14} CO molecules per second. Calculate the quantum efficiency for the reaction.

SOLUTION :**Formula used**

$$\phi = \frac{\text{No. of molecules reacted}}{\text{No. of einsteins absorbed}}$$

Quantities given

$$\text{No. of molecules of CO produced} = 3 \times 10^{14}$$

$$\text{No. of quanta absorbed} = \frac{\text{Total energy}}{\frac{h c}{\lambda}}$$

$$= \frac{0.001 \times 3100 \times 10^{-8}}{6.02 \times 10^{-27} \times 3 \times 10^{10}} \text{ J}$$

$$= \frac{0.001 \times 3100 \times 10^{-8} \times 10^7}{6.02 \times 10^{-27} \times 3 \times 10^{10}} \text{ erg}$$

$$= 1.56 \times 10^{15}$$

Substitution of values

$$\phi = \frac{3 \times 10^{14}}{1.56 \times 10^{15}}$$

$$= 0.192$$

SOLVED PROBLEM 27. In the photochemical reaction between Cl_2 and H_2 , 2.5×10^{-10} mole of chlorine have been converted to hydrochloric acid by irradiation with light of 4500 \AA . What is the quantum efficiency of the reaction if light absorbed in the system is $3.0 \times 10^{-15} \text{ kJ}$?

SOLUTION : (i) To calculate the no. of photons absorbed

Formula used

$$\text{No. of photons absorbed} = \frac{\text{Total energy absorbed}}{\text{Energy of a photon}}$$

Quantities given

$$\text{Total energy absorbed} = 3.0 \times 10^{-15}$$

$$\begin{aligned} \text{Energy of a photon} &= \frac{hc}{\lambda} = \frac{6.62 \times 10^{-27} \times 3 \times 10^{10}}{4500 \times 10^{-8}} \\ &= 4.41 \times 10^{-19} \text{ J} \end{aligned}$$

Substitution of values

$$\begin{aligned} \text{No. of photons absorbed} &= \frac{3.0 \times 10^{-15} \text{ J}}{4.41 \times 10^{-19} \text{ J}} \\ &= 6.80 \times 10^4 \end{aligned}$$

(ii) To calculate the quantum efficiency

Formula used

$$\text{Quantum efficiency} = \frac{\text{No. of molecules reacted}}{\text{No. of photons absorbed}}$$

Quantities given

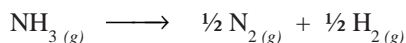
$$\text{No. of photons absorbed} = 6.80 \times 10^4$$

$$\begin{aligned} \text{No. of molecules of } \text{Cl}_2 \text{ reacted} &= 2.50 \times 10^{-10} \times 6.02 \times 10^{23} \\ &= 1.505 \times 10^{14} \end{aligned}$$

Substitution of values

$$\begin{aligned} \text{Quantum efficiency} &= \frac{1.505 \times 10^{14}}{6.80 \times 10^4} \\ &= 2.213 \times 10^9 \end{aligned}$$

SOLVED PROBLEM 28. In the photochemical reaction



with light at wavelength 2100 \AA it is found that 1940 J of energy decomposes 7.4×10^{-4} mole of NH_3 . Calculate the quantum yield.

SOLUTION : (i) To calculate the energy of a photon

Formula used

$$E = \frac{hc}{\lambda}$$

Quantities given

$$h = 6.62 \times 10^{-27} \text{ erg sec} \quad c = 3 \times 10^{10} \text{ cm sec}^{-1} \quad \lambda = 2100 \text{ \AA} = 2100 \times 10^{-8} \text{ cm}$$

Substitution of values

$$\begin{aligned} E &= \frac{6.62 \times 10^{-27} \times 3 \times 10^{10}}{2100 \times 10^{-8}} \\ &= 9.457 \times 10^{-12} \text{ erg} \\ &= 9.457 \times 10^{-19} \text{ J} \end{aligned}$$

(ii) To calculate the quantum efficiency**Formula used**

$$\phi = \frac{\text{No. of molecules reacted}}{\text{No. of photons absorbed}}$$

Quantities given

$$\begin{aligned} \text{No. of the molecules reacted} &= 7.4 \times 10^{-4} \text{ mole} \\ &= 7.4 \times 10^{-4} \times 6.02 \times 10^{23} \text{ molecules} \end{aligned}$$

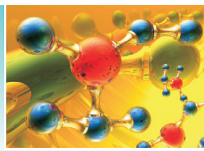
$$\begin{aligned} \text{No. of photons absorbed} &= \frac{\text{Energy absorbed}}{\text{Energy per photon}} \\ &= \frac{1940 \text{ J}}{9.457 \times 10^{-19} \text{ J}} \\ &= 2.0485 \times 10^{21} \end{aligned}$$

Substitution of values

$$\begin{aligned} \phi &= \frac{7.4 \times 10^{-4} \times 6.02 \times 10^{23}}{2.0485 \times 10^{21}} \\ &= \mathbf{0.217} \end{aligned}$$

ADDITIONAL PRACTICE PROBLEMS

- In a certain experiment irradiation of biacetyl gas with UV radiations (2537 \AA) for 5 hours produced 6.33 mole per litre of CO. The intensity of the radiation absorbed by acetyl gas was $1.71 \times 10^{-6} \text{ J per second}$. Calculate the quantum yield of CO.
Answer. 0.97
- Calculate percentage of light transmitted through 5 mm length of a liquid of absorption coefficient 2.5.
Answer. 28.65%
- A 2 mm thick plate of a material transmits 70% of the incident light. Calculate the percentage of light transmitted if the thickness of the plate is 0.5 mm.
Answer. 91.47
- Calculate the energy of one photon of light of wavelength 5000 \AA . Will it be able to break a bond in a diatomic molecule which absorbs this photon and has a bond energy equal to 300 kJ mol^{-1} ?
Answer. $3.972 \times 10^{-19} \text{ J}$; No
- Calculate the energy of a photon corresponding to wave length 360 nm. Given : velocity of light = $3 \times 10^8 \text{ m sec}^{-1}$; $h = 6.62 \times 10^{-34} \text{ J sec}^{-1}$.
Answer. $5.525 \times 10^{-19} \text{ J}$
- A certain system absorbs 3×10^{16} quanta of light per second. Calculate the quantum efficiency of the process if 2.00×10^{-3} mole of the reactant was found to have reacted in 10 minutes.
Answer. 66.92
- What percentage of light will be transmitted through two cells put together in the path of light, if their individual transmissions are 60% and 30%.
Answer. 18%
- A system absorbs 9×10^{20} quanta of light per second. The number of moles of reactant decomposed in one second is 2.98×10^{-4} . Calculate the quantum efficiency of the system.
Answer. 0.2 molecule per quantum
- A 0.55 mm thick glass is found to have a transmission of 70% for light of wavelength 2537 \AA . What will be thickness of the glass if transmission is 40.7%.
Answer. 2.0 mm



SI Units

COMMON SYSTEMS OF MEASUREMENTS

There are two common systems of measurement.

(1) Metric System

This is a decimal system of weights and measures originally based on the meter as the unit of length and the kilogram as the unit of mass.

(2) SI System

The International system of units was adopted by the 11th General Conference of Weights and Measures in 1960. The **SI units are widely used but they have not been fully accepted by the scientific community.**

In fact, metric system is still used in most countries. The American textbooks make use of the metric system freely. May be that America reverts to the metric system over the years.

In this book we have used the metric units throughout. However, at several places the SI units have also been used as we feel that in the present state of confusion the student should be conversant with both types of units. Here, we will discuss the metric and the SI units as also the conversion factors.

TABLE 1. SI BASE UNITS

Physical Quantity	Unit	Symbol
Length	meter	m
Mass	kilogram	kg
Time	second	s
Temperature	kelvin	K
Electric current	ampere	A
Number of particles	mole	mol

SI UNITS OF LENGTH

The SI unit of length is the meter (m). Fractions and multiples of SI units are named by adding appropriate prefixes. The commonly used metric length units are listed in Table 2.

TABLE 2. COMMON METRIC LENGTH UNITS

Unit	Symbol	Relation
meter	m	
kilometer	km	$1 \text{ km} = 10^3 \text{ m}$
decimeter	dm	$1 \text{ dm} = 10^{-1} \text{ m}$
centimeter	cm	$1 \text{ cm} = 10^{-2} \text{ m}$
millimeter	mm	$1 \text{ mm} = 10^{-3} \text{ m}$
micrometer	μm	$1 \mu\text{m} = 10^{-6} \text{ m}$
nanometer	nm	$1 \text{ nm} = 10^{-9} \text{ m}$
picometer	pm	$1 \text{ pm} = 10^{-12} \text{ m}$
angstrom	\AA	$1 \text{\AA} = 10^{-8} \text{ cm} = 10^{-10} \text{ m}$

Even though the unit **angstrom** (\AA) is not part of the SI system, it is still used for distances between atoms. Currently, the interatomic distances are sometimes reported in units of nanometers (nm) or picometer (pm).

$$\begin{aligned}1 \text{ nm} &= 10 \text{ \AA} \\1 \text{ pm} &= 10^{-2} \text{ \AA} \\1 \text{ nm} &= 10^{-3} \text{ pm}\end{aligned}$$

It may be noted that **the metric symbols are not changed into plurals**. Thus five centimeters of length is written as

Correct

5 cm

Incorrect

5 cm. 5 c.m. 5 cms

SI UNITS OF VOLUME

The derived SI unit of volume is

Cubic meter m^3

This is the volume of a cube that is 1 meter on each edge. The related units of volume which are also used are :

Cubic centimeter cm^3

Cubic decimeter dm^3

Another common measure of volume is the litre (a non-SI unit) which is denoted by **L** (ℓ or l).

A liter is the volume occupied by a cube 10 cm on edge. That is,

$$1 \text{ L} = (10 \text{ cm})^3 = 1000 \text{ cm}^3$$

Also

$$1 \text{ L} = 1000 \text{ mL}$$

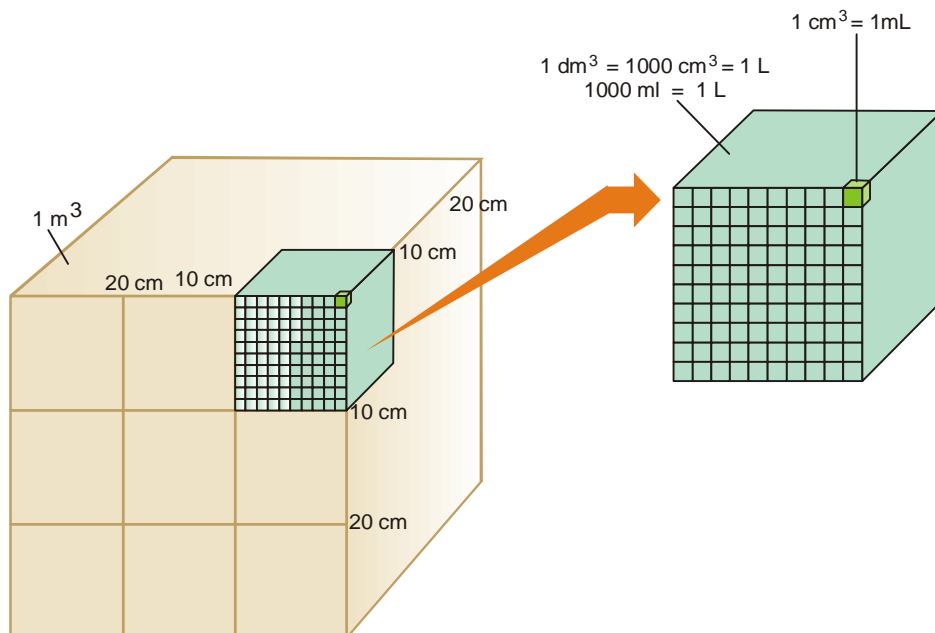


Figure 1
Relationship between length and volume.

Therefore $1000\text{ mL} = 1000\text{ cm}^3$

$$1\text{ mL} = 1\text{ cm}^3(\text{cc})$$

Hence **the volume units millilitre (mL) and cubic centimeter (cc) can be used interchangeably.** It may again be stated that metric symbols are not changed into plurals. Thus,

Correct

mL (or ml)

Incorrect

mLs (mls), m.l., ml.

SI UNIT OF TEMPERATURE

The series of markings on a thermometer which read temperature is called a **temperature scale**.

A temperature scale in which 0° is assigned to the freezing point of pure water and 100° to the boiling-point is known as the **Celsius scale**. The temperatures are expressed in **degrees Celsius ($^\circ\text{C}$)**. **Room temperature on the celsius scale is taken to be 25°C .** The celsius scale is not a part of the SI system. Since it is widely used in scientific literature, it is difficult to abandon it.

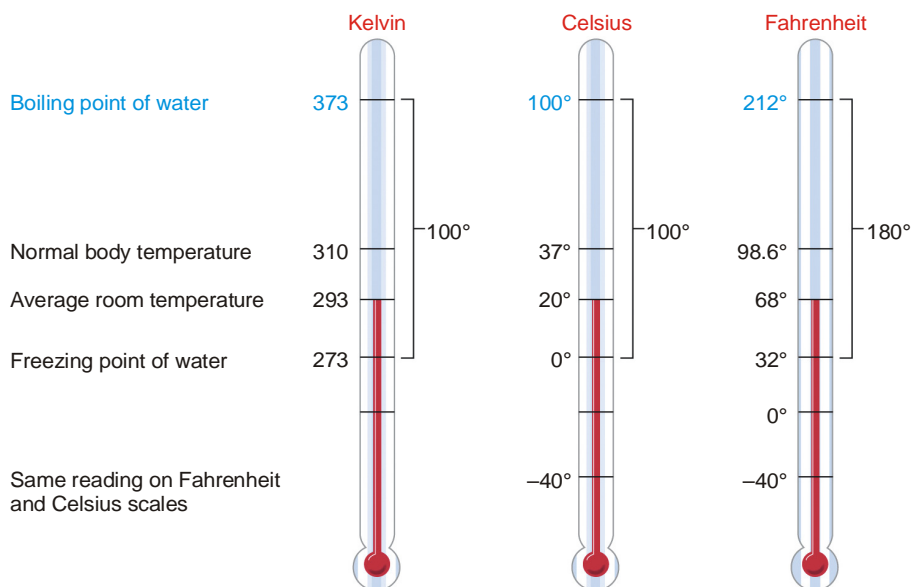
The SI system uses the Kelvin scale. A degree on the Kelvin scale has the same magnitude as a degree on the celsius scale but zero on the Kelvin scale equals -273.15°C . Thus the temperature (0 K) is often referred to as the **absolute zero**. Celsius and Kelvin temperature are related as

$$\text{K} = ^\circ\text{C} + 273.15$$

$$^\circ\text{C} = \text{K} - 273.15$$

It may be noted that the unit for temperature on the Kelvin scale is **K and not $^\circ\text{K}$** . This notation has been approved by IUPAC and is now used by chemists all over the world. **Thus it may be noted that a degree sign ($^\circ$) is not used with the Kelvin scale.**

On the **Fahrenheit scale** pure water freezes at 32° and boils at 212° . Thus 100° celsius equals $212 - 32 = 180$ Fahrenheit degrees. Celsius and Kelvin temperatures are related by the following equations.



■ **Figure 2**

A comparison of Kelvin, Celsius, and Fahrenheit scales.

$$^{\circ}\text{C} = \frac{5}{9} (^{\circ}\text{F} - 32)$$

$$^{\circ}\text{F} = \frac{9}{5} ^{\circ}\text{C} + 32$$

Using these relations it is easy to convert a temperature reading from Fahrenheit to Celsius and *vice versa*.

UNITS OF MASS AND WEIGHT

A beginner is apt to confuse mass with weight. The two quantities are related but are not equal. The **mass** (m) of an object is the amount of matter contained in that object. Mass is an invariant property of an object. It is the same on the surface of the earth as on the surface of the moon.

The **weight** (w), on the other hand, is force and not mass. It can be calculated by multiplying mass with the gravitational acceleration (g). That is,

$$w = m \times g$$

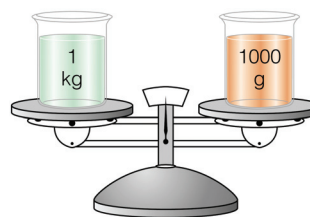
The gravitational pull on an object decreases as the object is moved farther from the centre of the earth. Thus astronauts lose weight as they move higher and higher from earth. It follows, therefore, that **even though the weight of an object can vary at different places, its mass stays the same**.

Although mass and weight are not the same, the two terms are used interchangeably even by the scientific community. This is so because an object of a certain mass weigh with virtually the same anywhere on the earth. Known masses, for example, are measured by a process termed 'weighing' with a balance.

The basic unit of mass in the metric system (or SI system) is gram. The commonly used units based on the gram are listed in Table 3.

TABLE 3. COMMONLY USED METRIC WEIGHT AND MASS UNITS

Unit	Symbol	In terms of grams
gram	g	
Kilogram	kg	$1 \text{ kg} = 10^3 \text{ g}$
milligram	mg	$1 \text{ mg} = 10^{-3} \text{ g}$
microgram	μg	$1 \mu\text{g} = 10^{-6} \text{ g}$



The British system of metric weights is also used by chemists in which

ounce (1 lb = 16 oz) $1 \text{ lb} = 453.6 \text{ g}$

pound 1 lb $2.205 \text{ lb} = 1 \text{ kg}$

ton (1 ton = 2000 lb)

It may be noted that metric units are not pluralised. Thus,

Correct

2 g

Incorrect

2gs, 2gms, 2g.m.

UNITS OF FORCE

Force (F) is defined as the product of mass (m) and acceleration (a).

$$\mathbf{F} = m \times a$$

Acceleration is the change in velocity (v) per unit time (t). Velocity is the change in distance (l) per unit time. Using SI base units, we can derive the unit for acceleration.

		UNIT
distance	l	m
velocity $\left(\frac{\text{distance}}{\text{time}}\right)$	v	$\frac{m}{s}$
acceleration $\left(\frac{\text{change in velocity}}{\text{time}}\right)$	a	$\frac{m}{s^2}$

The derived SI unit for force, then, is kg ms^{-2} . The unit is called **newton** and has the symbol N. Thus,

$$1 \text{ N} = 1 \text{ kg ms}^{-2}$$

UNITS OF WORK AND HEAT ENERGY

Work has been defined as the product of the force and the distance through which it operates

$$w = f \times d$$

Because force is expressed in newtons and distance in meters, **the SI units of work and energy is the newton-meter**. It is also called **Joule (J)**.

$$1 \text{ J} = 1 \text{ Nm}$$

Heat is energy that flows from one object to another because of a temperature difference between the objects. The quantity of heat transferred is best expressed in joules. But it is often given in **calories (cal)**. One calorie is defined as exactly 4.184 joules. Thus,

$$1 \text{ cal} = 4.184 \text{ J}$$

One calorie of energy will raise the temperature of 1 g of liquid water by 1°C . *The calorie is a non-SI unit, but like the joule it can be used for any form of energy.* The calorie written with a capital C is equal to one kilocalorie, 1000 calories. Thus,

$$1 \text{ C} = 1000 \text{ cal}$$

UNITS OF PRESSURE

Pressure is defined as the force per unit area exerted on a surface. That is,

$$P = \frac{F}{A}$$

Thus we can determine the SI unit for pressure as :

	UNIT
Force F	kg ms^{-2} or N
Area A	m^2
Pressure $\frac{P}{A}$	$\text{kg m}^{-1} \text{s}^{-2}$ or Nm⁻²

The SI unit Nm^{-2} is named **pascal** and given the symbol **Pa**.

Three other units which have been traditionally used are :

atmosphere, symbol **atm**, is defined as the pressure exerted by a column of mercury 760 mm in height at 0°C .

torr, symbol **Torr**, is defined as the pressure exerted by a 1 mm column of mercury at 0°C.

millimeter of mercury or mm Hg, which is the height in millimeters of mercury that the pressure can support.

The various units of pressure are related as

$$1 \text{ atm} = 760 \text{ Torr} = 76 \text{ mm Hg} = 1.013 \times 10^5 \text{ Pa}$$

The three non-SI units *viz.*, Torr and mm Hg are still commonly used in current practice and it will take quite some time before the scientific community adopts the SI unit Pa.

UNITS OF DENSITY

One of the physical properties of a solid, a liquid, or a gas is its density (d). **Density is defined as mass per unit volume.** This may be expressed mathematically as

$$d = \frac{m}{V}$$

By using the base SI units and remembering that the unit for volume is m^3 , we can derive the SI unit for density.

$$\frac{\text{kg}}{\text{m}^3} \text{ or } \text{kg m}^{-3}$$

The other units of density commonly used are

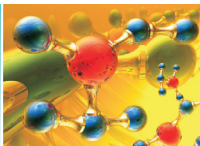
$$\text{g cm}^{-3} \text{ or } \text{g ml}^{-1} \text{ for liquid or solid densities}$$

$$\text{g L}^{-1} \text{ or } \text{g dm}^{-3} \text{ for gas densities}$$

The term **specific gravity is the ratio of the density of a substance to the density of a reference substance.** The reference substance for solids and liquids is usually water.

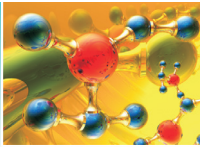
$$\text{sp gr} = \frac{\text{density of a substance}}{\text{density of reference substance}}$$

Specific gravity, being the ratio of two densities has no units.

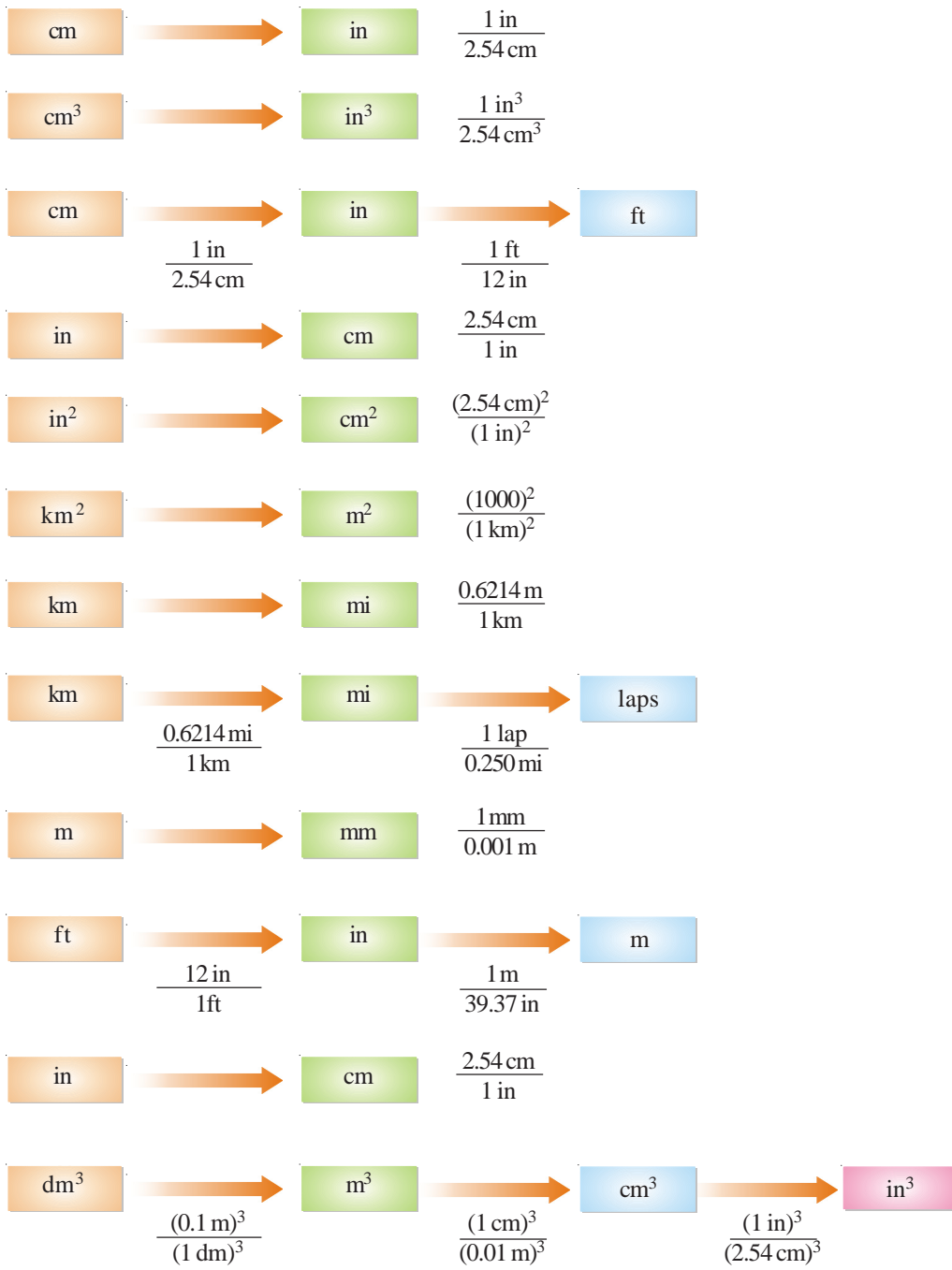


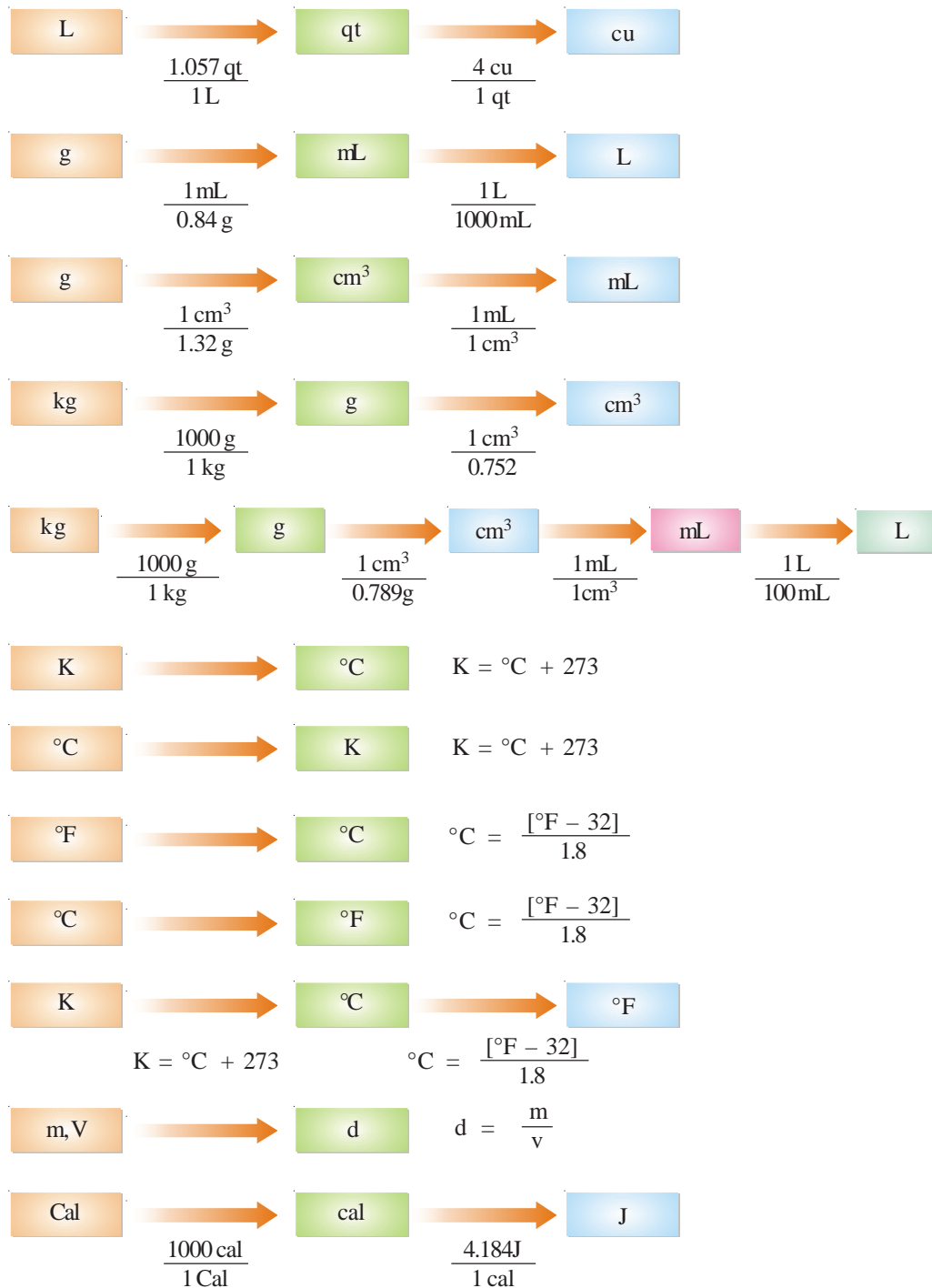
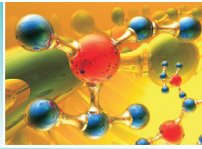
Physical Constants

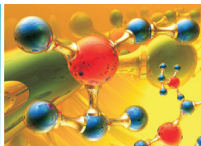
Quantity	Symbol	Traditional units	SI units
Atomic mass unit ($\frac{1}{12}$ th mass of ^{12}C atom)	amu	$1.6606 \times 10^{-24} \text{ g}$	$1.6606 \times 10^{-27} \text{ kg}$
Avogadro's number	N	6.022×10^{23}	6.022×10^{23} particles/mol
Bohr radius	a_0	0.52918 \AA	$5.2918 \times 10^{-13} \text{ m}$
Boltzmann constant	k	$1.3807 \times 10^{-16} \text{ erg/K}$	$1.3807 \times 10^{-23} \text{ J/K}$
Charge-to-mass ratio of electron	e/m	$1.7588 \times 10^8 \text{ Coulomb/g}$	$1.7588 \times 10^{11} \text{ C/kg}$
Electron rest mass	m_e	$9.1095 \times 10^{-28} \text{ g}$	$9.1095 \times 10^{-31} \text{ kg}$ 0.00054859 amu
Faraday constant	F	$96,487 \text{ coulombs/mole}^{-1}$	$96,487 \text{ J/V mol}^{-1}$
Gas constant	R	$0.08206 \frac{\text{L atm}}{\text{mol K}}$	$8.3145 \frac{\text{Pa dm}^3}{\text{mol K}}$
Gravitational acceleration	g	980.6 cm/s^2	9.806 m/s^2
Molar volume (STP)	V_m	22.414 L/mol	$22.414 \times 10^{-3} \text{ m}^3/\text{mol}$
Neutron rest mass	m_n	$1.67495 \times 10^{-24} \text{ g}$	$1.67495 \times 10^{-27} \text{ kg}$ 1.008665 amu
Planck's constant	h	$6.6262 \times 10^{-27} \text{ erg sec}$	$6.6262 \times 10^{-27} \text{ J sec}$
Proton rest mass	m_p	$1.6726 \times 10^{-27} \text{ erg sec}$	$1.6726 \times 10^{-27} \text{ kg}$ 1.007277 amu
Velocity of light (in vacuum)	c	$2.9979 \times 10^{10} \text{ cm/s}$ $186,281 \text{ miles/s}$	$2.9979 \times 10^8 \text{ m/s}$
Rydberg constant	R_z	$3.289 \times 10^{15} \text{ cycles/s}$ $2.1799 \times 10^{-11} \text{ erg}$	$1.0974 \times 10^7 \text{ m}^{-1}$ $2.1799 \times 10^{-18} \text{ J}$



Conversion Factors







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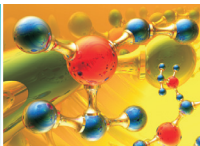
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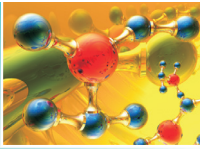
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Physical Constants

Quantity	Symbol	Traditional units	SI units
Atomic mass unit ($\frac{1}{12}$ th mass of ^{12}C atom)	amu	$1.6606 \times 10^{-24} \text{ g}$	$1.6606 \times 10^{-27} \text{ kg}$
Avogadro's number	N	6.022×10^{23}	6.022×10^{23} particles/mol particles/mol
Bohr radius	a_0	0.52918 \AA	$5.2918 \times 10^{-13} \text{ m}$
Boltzmann constant	k	$1.3807 \times 10^{-16} \text{ erg/K}$	$1.3807 \times 10^{-23} \text{ J/K}$
Charge-to-mass ratio of electron	e/m	$1.7588 \times 10^8 \text{ Coulomb/g}$	$1.7588 \times 10^{11} \text{ C/kg}$
Electron rest mass	m_e	$9.1095 \times 10^{-28} \text{ g}$	$9.1095 \times 10^{-31} \text{ kg}$ 0.00054859 amu
Faraday constant	F	$96,487 \text{ coulombs/mole}^{-1}$	$96,487 \text{ J/V mol}^{-1}$
Gas constant	R	$0.08206 \frac{\text{L atm}}{\text{mol K}}$	$8.3145 \frac{\text{Pa dm}^3}{\text{mol K}}$
Gravitational acceleration	g	980.6 cm/s^2	9.906 m/s^2
Molar volume (STP)	V_m	22.414 L/mol	$22.414 \times 10^{-3} \text{ m}^3/\text{mol}$
Neutron rest mass	m_n	$1.67495 \times 10^{-24} \text{ g}$	$1.67495 \times 10^{-27} \text{ kg}$ 1.008665 amu
Planck's constant	h	$6.6262 \times 10^{-27} \text{ erg sec}$	$6.6262 \times 10^{-27} \text{ J sec}$
Proton rest mass	m_p	$1.6726 \times 10^{-27} \text{ erg sec}$	$1.6726 \times 10^{-27} \text{ kg}$ 1.007277 amu
Velocity of light (in vacuum)	c	$2.9979 \times 10^{10} \text{ cm/s}$ $186,281 \text{ miles/s}$	$2.9979 \times 10^8 \text{ m/s}$
Rydberg constant	R_z	$3.289 \times 10^{15} \text{ cycles/s}$ $2.1799 \times 10^{-11} \text{ erg}$	$1.0974 \times 10^7 \text{ m}^{-1}$ $2.1799 \times 10^{-18} \text{ J}$



Conversion Factors

